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# CONTENTS (continued)

# INVESTIGATION OF THE SYSTEM $Tl_2SO_4 - Na_2S - H_2O$ (20 AND 25°) BY MEANS OF SOLUBILITY, ANALYSIS OF THE SOLID PHASE, AND APPARENT VOLUME OF THE PRECIPITATE

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The given system was investigated because sulfides of the elements and, in particular thallium sulfide ($Tl_2S$) have now acquired great importance as semiconductors. According to literature data [1], thallium sulfides of various compositions exist: $Tl_2S$, $Tl_8S_7$, $Tl_2S_2$, $Tl_6S_7$, $Tl_4S_5$, $Tl_2S_3$, $Tl_2S_5$. The first stage of the investigation was therefore the determination of the formation conditions and composition of precipitates formed in an aqueous medium over the range of $S^{2-} : Tl^+$ ratios* from 0 to 3, i.e., including the ratios of the sulfides given above, with particular attention paid to the region where $Tl_2S$ exists. As a component of the system studied we took $Tl_2SO_4$, as the most accessible and cheapest thallium salt (the latter is extracted from raw material in the form of the sulfate). In addition, it was interesting to compare the results of an investigation of the system $Tl_2SO_4-Na_2S-H_2O$ (20 and 25°) with the results of an investigation of the system $TlNO_3-Na_2S-H_2O$ (20°) and $CH_3COOTl-Na_2S-H_2O$ (20°) obtained by other authors [2] and thus determine the effect of the anions $NO_3^-$, $CH_3COO^-$, and $SO_4^{2-}$ on the formation of $Tl_2S$. It also seemed reasonable to investigate the system $Tl_2SO_4-Na_2S-H_2O$ by the procedure presented below, in which one vessel is used for three purposes at the same time, namely, determination of the solubility and the composition of the solid phase and measurement of the apparent volume of the precipitate. This accelerated the work and saved reagents.

The work was also accelerated and the accuracy increased as the solid phase was merely washed with a suitable solvent before analysis instead of being pressed to remove the liquid phase and weighed. In our case, the solid phase was washed with acetone or hydrogen sulfide solution**, in which it is insoluble. In order to accelerate and facilitate the washing of the solid phase a small amount of it was prepared or taken for analysis. After the solid phase had been washed, the whole of it or an aliquot part of it was analyzed.

## EXPERIMENTAL

The vessels for the investigation of the system $Tl_2SO_4-Na_2S-H_2O$ (20°) were 30 ml measuring tubes, 10-12 mm in diameter, which were closed with rubber stoppers and which were designed for the measurement of the apparent volume of precipitates by Tananaev's method [3]. These vessels were used at the same time to study the system by means of solubility and analysis of the solid phase. In the starting solution mixtures, the content of $Tl^+$ ions was kept constant at 0.001 g-ion/20 ml (or 0.05 g-ion/liter), while the amount of $S^{2-}$ ions was gradually increased over the range n = 0.05-3.00. The volume of the system equalled 20 ml. The following reaction must occur in the system investigated: $Tl_2SO_4 + Na_2S \rightarrow Tl_2S \downarrow + Na_2SO_4$ and according to this complete precipitation of the thallium as $Tl_2S$ should correspond to n = 0.5. Equilibrium was reached in the system investigated after manual mixing for 40 min by inversion of the vessels*** and standing for two days.**** Data obtained on the system $Tl_2SO_4-Na_2S-$    by the three given methods are presented in the table. Data on the apparent volume of the precipitates are given for 1-

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*The $S^{2-} : Tl^+$ ratio will be denoted by n.
**The water of crystallization in the solid phase was not determined in this case.
***For 20 min after the solutions had been mixed and for 20 min after the mixture had stood for a day.
****The time to reach equilibrium in the system was established by determination of the $SO_4^{2-}$ in the liquid phase.

Precipitate Volumes and Analyses of the Liquid (Solubility Determination) and Solid Phases in the System $Tl_2SO_4-Na_2S-H_2O$ (20 and 25°) (The starting solution mixtures had a constant $Tl^+$ content of 0.05 g-ion/liter)

| Experiment No. | $S^{2-}:Tl^+$ in starting mixture | Precipitate volume(ml) after | | Analysis of liquid phase included in precipitate, g-ion·$10^4$/20 and 50 ml | | | precipitate composition | | Analysis of solid phase, g-ion·$10^4$ | | precipitate composition | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 hr | 48 hrs | 1 hr | $S^{2-}$ | $Tl^+$ | $S^{2-}:Tl^+$ | formula | $S^{2-}$ | $Tl^+$ | $S^{2-}:Tl^+$ | formula |
| 1 | 0,05 | 0,20 | 0,12 | — | 0,50 / 2,00 | 1,09 / 3,78 | 0,47 / 0,53 | | 0,57 | 1,10 | 0,52 | |
| 2 | 0,20 | 0,70 | 0,55 | 2,2 | 5,0 / 3,99 | 11,0 / 7,09 | 0,45 / 0,56 | | — | — | — | |
| 3 | 0,40 | 1,10 | 0,90 | — | — / 4,99 | — / 8,65 | — / 0,58 | | 3,82 | 7,20 | 0,53 | |
| 4 | 0,50 | 1,24 | 1,09 | 5,0 | 12,5 / 5,00 | 25,0 / 10,0 | 0,50 / 0,50 | | 5,10 | 9,80 | 0,52 | |
| 5 | 0,55 | 1,33 | 1,21 | 5,0 | 12,7 / 5,99 | 25,0 / 10,0 | 0,51 / 0,60 | | 5,05 | 9,90 | 0,51 | |
| 6 | 0,60 | 1,40 | 1,25 | 5,0 | 13,0 / 5,48 | 25,0 / 10,0 | 0,52 / 0,55 | | 5,04 | 9,70 | 0,52 | |
| 7 | 0,80 | 1,30 | 1,20 | 4,9 | 12,6 / 5,91 | 25,0 / 10,0 | 0,50 / 0,59 | | 5,00 | 10,00 | 0,50 | |
| 8 | 0,875 | — | — | 4,8 | 12,4 / 5,13 | 25,0 / 10,0 | 0,50 / 0,51 | | 5,01 | 9,82 | 0,51 | |
| 9 | 0,90 | 1,32 | 1,21 | 4,8 | 12,2 / 5,13 | 25,0 / 10,0 | 0,49 / 0,51 | | — | — | — | |
| 10 | 1,00 | 1,30 | 1,19 | 4,7 | 11,8 | 25,0 | 0,47 | $Tl_2S$ | 5,03 | 9,67 | 0,52 | $Tl_2S$ |
| 11 | 1,16 | — | — | 4,7 | 12,5 / 6,19 | 25,0 / 10,0 | 0,50 / 0,63 | | 5,02 | 9,66 | 0,52 | |
| 12 | 1,20 | 1,31 | 1,20 | 4,6 | 12,0 | 25,0 | 0,48 | | 5,00 | 10,00 | 0,50 | |
| 13 | 1,25 | — | — | 4,6 | 13,2 / 6,35 | 25,0 / 10,0 | 0,53 / 0,63 | | 5,01 | 9,82 | 0,51 | |
| 14 | 1,50 | 1,31 | 1,20 | 4,4 | 13,7 | 25,0 | 0,55 | | 5,04 | 9,70 | 0,52 | |
| 15 | 1,55 | — | .— | 4,4 | 12,7 / 5,88 | 25,0 / 10,0 | 0,51 / 0,59 | | — | — | — | |
| 16 | 2,00 | 1,30 | 1,14 | 4,2 | 12,6 | 25,0 | 0,50 | | 5,01 | 9,82 | 0,51 | |
| 17 | 2,45 | | | 3,8 | 12,2 | 25,0 | 0,49 | | — | — | — | |
| 18 | 2,50 | | | 3,8 | 13,2 | 25,0 | 0,53 | | 5,02 | 9,84 | 0,51 | |
| 19 | 3,00 | | | 3,4 | 13,5 | 25,0 | 0,54 | | 5,02 | 9,66 | 0,52 | |

and 48-hr standing after mixing of the solutions. The liquid and solid phases were analyzed after they had been separated by filtration with a No. 4 glass filter funnel. The liquid phase was collected in a tube, which was placed under the narrow end of the filter funnel inside the suction flask.

Aliquot portions of the liquid phase were used to detect $Tl^+$ ions as $Tl_2S$ and $S^{2-}$ ions as CuS. The data in the table show that when there was an excess of $Tl^+$ ions in the solution (over the range of values of $\underline{n}$ from 0.0 to 0.5), the $S^{2-}$ ions passed completely into the precipitate. In this case, the excess of thallium ions was determined on an aliquot portion of the solution by precipitation as $Tl_2CrO_4$ [4] by the procedure developed by Bashilova [5]. When there was an excess of $S^{2-}$ ions in the solution, the whole of the thallium naturally passed into the precipitate ($n = 0.55-3.00$); in this case, the sulfur in the solution (the sum $S^{2-} + SO_4^{2-}$ was determined as $BaSO_4$ after oxidation of the $S^{2-}$ to $SO_4^{2-}$ ions with bromine water. The content of $S^{2-}$ ions in the solution was determined from the difference between the total sulfur content ($S^{2-} + SO_4^{2-}$ determined as $SO_4^{2-}$ ions, and the amount of $SO_4^{2-}$ from the $Tl_2SO_4$ in the starting mixture.

Thus, in the solubility method, the composition of the precipitate was determined from the difference between the components taken and those remaining in solution after precipitation. In addition, the composition of the precipitate was determined by direct analysis. For this purpose, the precipitate, which was collected almost completely

on the filter funnel by means of the liquid phase, was washed twice with moist acetone (when washing the precipitate free from $Tl_2SO_4$, i.e., when n = 0.0-0.5) or hydrogen sulfide solution (when washing the precipitate free from $Na_2S$, i.e., when n = 0.55-3.00). The precipitate on the filter funnel was then dissolved in 3-5 ml of perhydrol and this solution collected in another tube, placed under the end of the filter funnel inside the suction flask. The solution of the solid phase in perhydrol was diluted to 50 ml with water and the bulk of the $H_2O_2$ decomposed by evaporation of the solution to 25 ml. The $Tl^+$ was oxidized to $Tl^{3+}$ by the addition of bromine water to a pale yellow color. The excess bromine was removed by boiling, $Tl(OH)_3$ precipitated with ammonia, the precipitate collected by filtration, and the sulfur in the filtrate determined as barium sulfate. The precipitate of $Tl(OH)_3$ on the filter was dissolved in hot dilute $H_2SO_4$, the $Tl^{3+}$ reduced to $Tl^+$ (by the addition of $Na_2SO_3$ with subsequent removal of the $SO_2$ by evaporation of the solution), and the thallium determined as $Tl_2CrO_4$. At all values of n, the liquid phase contained $Na_2SO_4$, formed by the exchange reaction given above, but calculation showed (see table) that the precipitates did not contain $Na_2SO_4$.

The discrepancy between the point of complete precipitation of $Tl_2S$ and the theoretical value of n = 0.5 in the starting solution mixtures, i.e., the displacement to n = 0.55 (see table) could be the result of rapid oxidation of $Na_2S$ at the moment when the starting solutions were mixed. When the precipitate composition was calculated from the decrease in the components in the liquid phase, the ratio of $S^{2-}:Tl^+$ in the precipitate was somewhat greater than the theoretical value of n = 0.5 in some cases. This was also observed by other investigators [2]. Therefore, in order to check the results obtained, the system $Tl_2SO_4-Na_2S-H_2O$ (constant content of $Tl^+$ = 0.0025 g-ion/50 ml or 0.05 g-ion/liter) was investigated by a second procedure which we proposed and in which, in contrast to the first, vessels (50 ml measuring cylinders with a stirrer and a water trap) designed for the investigation of systems by solubility were used at the same time for investigating these systems by measurement of the apparent precipitate volume. In addition, the system $Tl_2SO_4-Na_2S-H_2O$ was investigated by the second procedure at 25° to determine whether a slight rise in temperature (from 20 to 25°) would affect the results. As the system was stirred with a stirrer with an electric motor in the second procedure, equilibrium was reached quite rapidly, namely, after stirring for 2 hr. When the precipitates had settled for an hour, their volumes were measured (third column in the table under the heading "Precipitate volume") and after the solid phase had been separated from the liquid phase by filtration, the latter was analyzed as in the first procedure, but with a change in the determination of the $S^{2-}$ ions. In this case only $S^{2-}$ ions were determined in order to eliminate the possible effects of $SO_3^{2-}$, $S_2O_3^{2-}$, and $SO_4^{2-}$ present in $Na_2S$ on the analysis results. The sulfide ions were separated as CuS (slight excess of $CuSO_4$, which was then fired to CuO, which was weighed. Data on the analysis of the liquid phase and the composition of the precipitate obtained by the second procedure are given in the table in the appropriate columns (lower figures). They show that complete precipitation of thallium in the system $Tl_2SO_4-Na_2S-H_2O$ corresponds to n = 0.5 in the starting solution mixtures, i.e., the formation of the precipitate $Tl_2S$.

## Discussion of Experimental Results

The data in the table show that the results of investigating the system $Tl_2SO_4-Na_2S-H_2O$ by means of solubility, analysis of the solid phase, and apparent volume of the precipitate both by the first procedure at 20° and by the second prodedure at 25° agree, and a slight difference in temperature has no effect on the results. In the system $Tl_2SO_4-Na_2S-H_2O$ (20 and 25°), which was investigated over the range n = 0-3, the composition of the precipitates corresponds to n = 0.5, i.e., the formula $Tl_2S$. Thus, the sulfide $Tl_8S_7$ (n = 0.875), $Tl_2S_2$ (n = 1), $Tl_6S_7$ (n = 1.16), $Tl_4S_5$ (n = 1.25), $Tl_2S_3$ (n = 1.5), and $Tl_2S_5$ (n = 2.5), which have been reported in the literature and obtained by fusion or other methods, are not formed in an aqueous medium. With an increase in n from zero, there is an increase in the precipitate volume, which reaches a maximum within the range n = 0.5-0.6. The precipitate volume then decreases regularly right up to n = 3. The difference between precipitate volumes measured 1 hr after mixing of the starting solutions and after two days was insignificant, i.e., recrystallization of the $Tl_2S$ precipitate with ageing proceeds quite rapidly, mainly in the first hour after formation of the precipitate and then slowly. A comparison of our results for the system $Tl_2SO_4-Na_2S-H_2O$ (20 and 25°) with the results for the systems $TlNO_3-Na_2S-H_2O$ (20°, n = 0.1-2.9) and $CH_3COOTl-Na_2S-H_2O$ (20°, n = 0.12-2.50), which were obtained by Nanobashvili, Shelia, and Ivanitskaya [2], who also used solubility, analysis of the solid phase, and the apparent volume of the precipitate, reveals the following: All three systems are similar in that the formation of only $Tl_2S$ was observed over the range of values of n studied.

The maximum on the precipitate volume curves for all the systems appeared in the same range n = 0.5-0.6 and the beginning of this maximum corresponded to n = 0.5, i.e., complete precipitation of the thallium as $Tl_2S$. A

difference in the anions at the given concentration did not affect the formation of $Tl_2S$. The systems differ in that the system with $Tl_2SO_4$ did not form colloidal solutions, while when the systems with $TlNO_3$ (n = 0.6-1.0) and $CH_3COOTl$ (n = 0.7-1.0) were investigated by means of the apparent precipitate volume, a colloidal solution was formed during the 24 hr after precipitation of $Tl_2S$. However, we should note that when the systems with $TlNO_3$ and $CH_3COOTl$ were investigated by means of solubility, the same authors [2] did not observe this colloid formation, which indicates only that the systems did not reach equilibrium in 24 hr when they were investigated by means of apparent precipitate volumes. A special investigation of the system $TlNO_3-Na_2S-H_2O$ (20°) which we carried out by the apparent precipitate volume method, showed that when the systems were mixed for a second time after standing for a day and then left for another day, the formation of colloids observed by the authors of [2] did not occur. The formation of colloids apparently would not occur in the system $CH_3COOTl-Na_2S-H_2O$ also with remixing after standing for a day and then standing for another day, i.e., if equilibrium were reached in this system. It seems to us that the procedure we propose for the investigation of chemical systems (the first) deserves attention for its simplicity and economy in time and reagents in the investigation of chemical systems which reach equilibrium comparatively quickly. In addition, this procedure may be modified to a micromethod, and replacement of manual mixing of the contents of the measuring tubes by mixing with an electric motor would make it possible to use the procedure proposed for the investigation of chemical systems requiring any time to reach equilibrium.

## SUMMARY

1. A method is proposed for the investigation of chemical systems by means of solubility, analysis of the solid phase, and apparent volume of the precipitate simultaneously in one vessel.

2. In the system $Tl_2SO_4-Na_2S-H_2O$ (20 and 25°), which was investigated by the procedure proposed, only one compound, namely, $Tl_2S$, was formed over the range of $S^{2-}$: $Tl^+$ ratios from 0 to 3 and the apparent volume of the precipitate first increased, reached a maximum within the range $S^{2-}$: $Tl^+$ = 0.5-0.6, and then decreased regularly.

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# KINETICS OF THERMAL DECOMPOSITION OF SOLIDS

## COMMUNICATION 2. THERMAL DECOMPOSITION OF SILVER CARBONATE

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The literature contains papers on the kinetics and mechanism of thermal decomposition of solids, including the case where the decomposition forms a mixture of gaseous reaction products [1, 2]*. Thus, Simpson, Taylor, and Anderson [2] studied the decomposition of ammonium bichromate by a manometric method, i.e., by measuring curves of the relation of pressure to time. In these experiments, the authors froze out one component from the gaseous mixture of decomposition products in individual cases. In the discussion of the results of our first communication [3], it was shown that the method of studying the kinetics of thermal decomposition of solids we described may be used to determine directly the rates of liberation of individual gases in a mixture formed by decomposition. In the present work we used this method to study the kinetics of decomposition of silver carbonate, which is a stepwise topochemical reaction. The thermal decomposition of silver carbonate forms silver oxide, which decomposes further to metallic silver in individual cases. In the general case, the gaseous decomposition products contain carbon dioxide and oxygen. We investigated the rates of liberation of these gases during the decomposition of silver carbonate preparations obtained by difficult methods.

## EXPERIMENTAL

The apparatus with which we measured the rates of liberation of gaseous products of the thermal decomposition of silver carbonate is illustrated in Fig. 1. A sample of the preparation was placed in the glass dish 1, which was suspended from the quartz spiral 2 with a glass fiber. From a second quartz spiral 3, with a sensitivity of approximately 3 times that of the spiral 2, was suspended a dish 4 with 600 mg of finely porous active charcoal. This ratio of the sensitivities of the two spirals gave optimal accuracy of the measurements. The changes in weight could be followed with two cathetometers with ocular micrometers. The tubes containing the quartz spirals had jackets for thermostating the spirals at 25° with water from an ultrathermostat and were connected through a trap 5. The whole apparatus was made from "Sial" heat-resistant glass. Apiezon L was used to grease all the taps and joints.

Experiments were carried out in the following way. After the sample had been weighed (~300 mg of silver carbonate), the lower end of the tube 8 containing the dish with active charcoal, was heated to 400° and the apparatus pumped out for 2 hr to a residual pressure of the order of $10^{-5}$ mm Hg. The instrument was then shut off from the vacuum part of the apparatus with tap 6 and the bottom of tube 8 and trap 5 cooled with liquid nitrogen. The thermal decomposition was carried out by placing the bottom of tube 7, which contained the dish with the sample, in a mixture of molten salts (42% of sodium nitrite, 51% of potassium nitrate, and 7% of sodium nitrate) [4], which was in an electric furnace, whose temperature was regulated with an accuracy of 1° with a contact thermometer. We checked that the carbon dioxide formed by decomposition of silver carbonate was frozen completely in trap 5 while the oxygen was absorbed completely and practically instantaneously by the active charcoal by separate experiments on the thermal decomposition of substances whose gaseous products consisted solely of pure components. As the loss in weight determined by spiral 2 was the sum of the weights of the carbon dioxide and oxygen formed during the experiment, and the increase in weight of the dish 4 represented the weight of oxygen liberated, from these data we could calculate the weight of carbon dioxide formed.

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*Such investigations were also carried out by O. Kadlets and V. Danesh in the Institute of Physical Chemistry of the Czechoslovakian Academy of Sciences.

Fig. 1. Diagram of apparatus for investigating thermal decomposition kinetics.



Fig. 2. Kinetics of thermal decomposition of a silver carbonate preparation of the first type for the following temperatures: 1) 303°; 2) 335° (the solid curves correspond to the liberation of carbon dioxide and the broken curve to oxygen).

The difference between this apparatus and that described in [3] was that the substance decomposed was not in a tube heated directly, but a dish suspended from a quartz spiral. This made it possible to determine the amounts of the gases formed simultaneously, but had all the drawbacks associated with the difficulties of heat transfer to a substance at low pressures. Therefore, in separate control experiments we used a thermocouple to measure the temperature of the silver carbonate during its decomposition.

On this apparatus we investigated the time dependence of the amounts of carbon dioxide and oxygen liberated during the thermal decomposition of silver carbonate samples obtained by different methods. The investigation of the thermal decomposition kinetics showed that there are essentially two types of silver carbonate preparations, which differ fundamentally in thermal decomposition kinetics. The first type includes silver carbonate preparations obtained by precipitation at 20° from aqueous solutions of silver nitrate with solutions of sodium carbonate (or bicarbonate) with concentrations of 1.0 to 0.005 M (from 1.0 to 0.015 M in the case of bicarbonate). The temperatures at which preparations of this type decomposed at rates suitable for measurement lay within the range of 280-340° and the silver oxide formed decomposed rapidly at these temperatures to metallic silver and oxygen. Similar silver carbonate preparations could be obtained by precipitation from silver nitrate solutions with silver bicarbonate solutions saturated with carbon dioxide at concentrations higher than 0.05 M. As an example, Fig. 2 gives curves of the time dependence of the amounts of gases liberated at 303, 325, and 335°, expressed in percents of the stoichiometric amounts of them in the starting material, for a silver carbonate preparation of the first type, which was prepared by precipitation from 0.2 M silver nitrate solution with sodium bicarbonate solution of the same concentration. The curves corresponding to the different gaseous thermal decomposition products differ only for the initial periods of the experiments. In these regions they are convex for carbon dioxide and concave for oxygen.

The second type of silver carbonate preparations, which decompose completely at much lower temperatures (below 200°), included preparations obtained by precipitation from more dilute solutions. Thus, in precipitation from equimolar solutions of silver nitrate with sodium carbonate solutions, the concentrations had to be less than 0.0015 M, with sodium bicarbonate solutions, less than 0.01 M, and when silver bicarbonate solution saturated with carbon dioxide was used for precipitation, less than 0.002 M. This type of silver carbonate preparation also included samples prepared from silver bicarbonate solutions in the following way. A suspension of silver carbonate in distilled water was saturated with carbon dioxide and the silver carbonate dissolved to form a silver bicarbonate solution. The bicarbonate solution was filtered and placed in a desiccator, which was evacuated. Over a period of a day, the silver bicarbonate decomposed slowly at room temperature to form small crystals of silver carbonate [5]. Samples prepared in this way underwent thermal decomposition below 200°. The decomposition products were silver oxide and carbon dioxide. Hardly any oxygen was liberated. Figure 3 shows thermal decomposition curves for a preparation of the second type, obtained by other methods. Dissolving silver carbonate in aqueous ammonia solutions yielded an ammoniate, from a solution of which silver carbonate was reprecipitated by carbon dioxide. Figure 4 gives curves of the kinetics of carbon dioxide liberation during the decomposition of the preparation obtained at various temperatures. The general form of these curves differs from that of curves for the thermal decomposition of lead carbonate [3] only in the convexity in the narrow initial region, which was probably caused by an induction period due to poor heat transfer.

Fig. 3. Curves of the kinetics of carbon dioxide liberation during thermal decomposition of a silver carbonate preparation of the second type, obtained from silver carbonate: 1) at 167°; 2) at 194°; 3) at 221°.
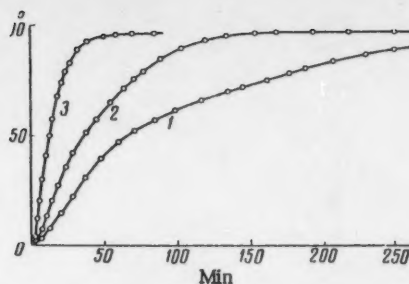


Fig. 4. Curves of the kinetics of carbon dioxide liberation during thermal decomposition of a silver carbonate preparation of the second type obtained from silver ammoniate: 1) at 198°; 2) at 221°; 3) at 270°.
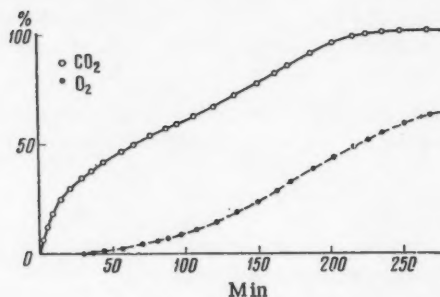


Fig. 5. Curves of the kinetics of thermal decomposition at 303° of a silver carbonate preparation which was precipitated in the intermediate concentration range.

A common characteristic of the formation of preparations of the second type was the fact that they were obtained from homogeneous solutions. When a dilute silver nitrate solution was mixed with sodium carbonate or bicarbonate solution, the solution remained clear for some time and the silver carbonate formed slowly from a homogeneous solution.

By precipitating silver carbonate with solutions of intermediate concentrations lying between the concentration ranges corresponding to preparations of the first and second types, we obtained samples whose properties were intermediate between those of the two types of silver carbonate preparations. Thus, Fig. 5 gives curves of the decomposition kinetics of silver carbonate prepared by precipitation with 0.04 M solutions of silver nitrate and sodium bicarbonate saturated with carbon dioxide. Figure 6 (curve 1) gives analogous data for the thermal decomposition of a silver carbonate preparation obtained from 0.01 M solutions of silver nitrate and sodium bicarbonate. As Figs. 5 and 6 show, the rate of oxygen liberation decreased to the same extent as the rate of carbon dioxide increased with a change from preparations of the first type to those of the second type.

The presence of indifferent electrolytes during precipitation also had a great effect on the properties of silver carbonate preparations during thermal decomposition. Curve 2 in Fig. 6 shows the thermal decomposition of an analogous preparation, which was precipitated in a solution with a sodium nitrate concentration of 0.1 M. No oxygen was liberated in this case.

As has been mentioned already, in individual cases we studied the effect of poor heat transfer on the temperature of a silver carbonate sample in the dish suspended from the quartz spiral. From a comparison of kinetic curves of oxygen liberation for preparations contained in dishes and preparations placed at the bottom of the tube 7 in the electric furnace at the same temperature, we estimated the temperature reduction caused by poor heat transfer to samples in dishes and obtained a value of 3-5°.

As silver salts are known to be sensitive to light, all operations with silver carbonate preparations were carried out in nonactinic red light. In addition, we studied the effect of light on the properties of silver carbonate preparations. As the curves in Fig. 7 show, it was found that preliminary irradiation of the preparations with ultraviolet light from a quartz mercury lamp had an appreciable effect on the thermal decomposition kinetics; it had a somewhat greater effect on the rate of silver oxide decomposition. However, the effect of irradiation was weaker than that of a change in the silver carbonate preparation conditions.
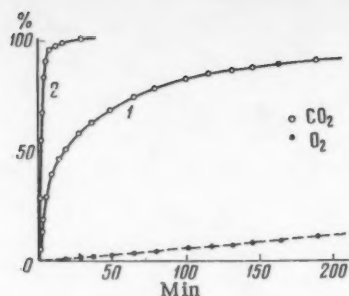
Fig. 6. Curves of the kinetics of thermal decomposition at 303° of silver carbonate preparations obtained by precipitation from 0.01 M solutions of $AgNO_3$ and $NaHCO_3$: 1) in the absence of $NaNO_3$; 2) in the presence of $NaNO_3$.
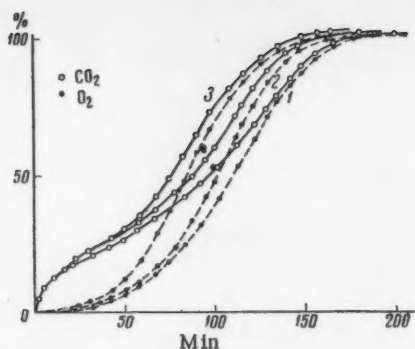


Fig. 7. Curves of the kinetics of thermal decomposition at 303° of a silver carbonate preparation obtained by precipitation from 0.2 M solutions of $AgNO_3$ and $NaHCO_3$: 1) without preliminary irradiation; 2) irradiation for 10 hr; 3) irradiation for 24 hr with ultraviolet light.

## Discussion of Experimental Results

The most important experimental fact is the existence of two types of silver carbonate preparations which differ sharply in thermal decomposition kinetics. It is therefore most interesting to consider possible reasons for the difference in preparations of the first and second types.

X-ray structural investigations showed that the crystallographic structure of the two types of silver carbonate preparations was the same. Preparations of the first and second types did not differ in chemical composition, which within the limits of accuracy of analytical methods, corresponded to the stoichiometric ratio of the elements for the formula $Ag_2CO_3$. Likewise, the difference in the properties of the silver carbonate preparations could not be explained by their dispersion as the relatively high dispersed preparations of the first type decomposed much more slowly at the same temperature than less dispersed preparations of the second type, which were obtained by precipitation from more dilute solutions.

Silver carbonate preparations of the first type with a lower thermal decomposition rate were obtained by precipitation from more concentrated solutions containing the ions $Na^+$ and $NO_3^-$, corresponding to one of the products of the exchange reaction. Higher adsorption or entrainment of ions during crystallization are probable under these conditions. However, the preparation of silver carbonate samples in the presence of a ten-fold excess of the indifferent electrolyte $NaNO_3$ led to an appreciable increase in the thermal decomposition rate rather than a decrease (Fig. 6). Thus, possible increased adsorption or entrainment of $Na^+$ and $NO_3^-$ ions cannot be the main reasons for the difference in the properties of silver carbonate preparations of the first and second types. Some results of other authors who studied the thermal decomposition of silver carbonate indicate a difference in the properties of silver carbonate preparations obtained by different methods [5, 6].

One factor which could be of decisive importance to the properties of silver carbonate preparations is the precipitation rate, which depends on the supersaturation of the solutions from which silver carbonate crystals are formed. It may be surmised that under difficult crystallization conditions when extremely dilute solutions are used for precipitation, silver carbonate preparations of the second type are formed with a more defective crystal structure, and for this reason decompose at lower temperatures.

In the formation of silver carbonate preparations of the first type by precipitation, by mixing more concentrated solutions, for example, of silver nitrate and sodium bicarbonate, the concentration conditions created in the final stage of precipitation are typical of those for the formation of silver carbonate preparations of the second type. Therefore preparations of the first type obtained by precipitation may contain a certain amount of preparations of the second type or a certain volume of a defective crystal structure. It may be visualized that the amount of silver carbonate in a preparation of the first type which decomposes more rapidly and at a lower temperature than the remaining amount of silver carbonate which really belongs to the first type will be proportional to this volume.
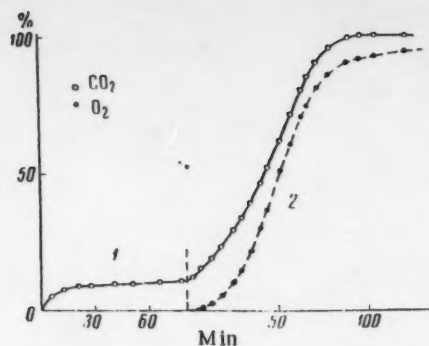
Fig. 8. Kinetic curves of stepwise decomposition of a silver carbonate preparation of the first type: 1) at $212°$; 2) at $325°$.

These arguments were confirmed by an experiment on the stepwise thermal decomposition of a silver carbonate preparation of the first type, obtained by precipitation from 0.2 M solutions of silver nitrate and sodium bicarbonate. The thermal decomposition curves are given in Fig. 8. The first stage of the thermal decomposition of the preparation was carried out for 80 min at $212°$ and was typical of the fast decomposition of preparations of the first type. Only carbon dioxide was liberated in this stage of the decomposition. The second stage of the thermal decomposition corresponded to the temperature $325°$, at which preparations of the first type decompose at quite a high rate with the liberation of carbon dioxide and oxygen. From the limiting amounts of carbon dioxide liberated in the first and second stages of the thermal decomposition it may be estimated that the crystals of the silver carbonate preparation of the first type studied contained 10-12% of defect structure. This contamination by a preparation of the second structure caused the more complex undulating form of the kinetic curves of carbon dioxide liberation obtained for silver carbonate preparations of the first type (Figs. 2 and 7).

## SUMMARY

1. A new method is described which makes it possible to study consecutive and side reactions in the thermal decomposition of solids.

2. On the example of the thermal decomposition of silver carbonate preparations obtained under different conditions, it was shown that there are two limiting types of preparations of the same chemical and crystallographic structure, which differ sharply in thermal decomposition kinetics.

3. The difference in the properties of the preparations may be connected with the presence of defects in the crystal structure.

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# ADSORPTION PROPERTIES AND SECONDARY POROUS STRUCTURE
# OF ADSORBENTS WITH A MOLECULAR SIEVE ACTION

## COMMUNICATION 1. INDUSTRIAL SAMPLES OF SYNTHETIC ZEOLITES

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Synthetic zeolites are finding increasing application in modern technology as selective and highly efficient adsorbents for the thorough drying of gases and the separation of mixtures of substances in gaseous and liquid phases. The sharp selectivity of their adsorption properties is based on the so-called molecular sieve action, i.e., the penetration or nonpenetration of the adsorbed molecules through the narrower entrances or "windows" leading to wider spaces formed in the crystal structure of the dehydrated zeolites, which constitute the main volume of the adsorption space. Zeolites readily adsorb substances whose molecules are able to pass through the windows into the spaces. The adsorption capacity of zeolites for substances with larger molecules for which the windows are impassable is insignificantly low over a wide range of relative pressures. Synthetic zeolites are therefore often called "molecular sieves." In a review article, Barrer gave a classification of natural and synthetic zeolites with respect to their molecular sieve action and general data on their crystal structure, adsorption properties, and practical application for various purposes [1].

Linde molecular sieves 4A, 5A, 10X, and 13X are industrial adsorbents based on crystalline sodium or potassium aluminosilicates. Zeolite crystals of microscopic size, obtained by hydrothermal synthesis and washed carefully*, are formed into granules with binding agents and strongly dehydrated to give the industrial adsorbents. These granules, which consist of aggregates of highly disperse zeolite crystals in contact and are truly molecular sieves, are characterized by a definite total outer surface of the crystals and gaps between them, forming a secondary porous structure. The vapors of substances whose molecules are unable to penetrate into the adsorption space of the molecular sieves will therefore be adsorbed on the outer surface of the highly disperse crystals and at higher relative pressures one might expect capillary condensation in the gaps between the crystals, i.e., in the secondary porous structure.

While the adsorption of gases and vapors by the molecular sieves themselves is selective in accordance with the critical dimensions of the molecules adsorbed [1], adsorption on the outer surface of the crystals and capillary condensation of vapors in the gaps between them are not selective in character. This nonspecific component of sorption may be of relatively greater importance if hydrothermal synthesis is incomplete and especially if aluminosilica gel is not removed adequately during washing. Thus, nonspecific adsorption in the secondary porous structure of the granules, which must occur on the outer surface of crystals of molecular sieves, traces of aluminosilica gels, and binders, will have a negative effect on the completeness of separation of substances, produced by the molecular sieve action.

The purpose of the present work was a study of some characteristics of the adsorption properties of typical samples of industrial synthetic zeolites and their secondary porous structure.

## EXPERIMENTAL

As subjects for the investigation we used industrial samples of Linde molecular sieves 4A (designated as MS-4A) and 5A (designated as MS-5A) in the form of granules with a mean diameter of ~3.2 mm and a length of 4-8 mm.
* With exchange of $Na^+$ for $Ca^{++}$ where necessary.
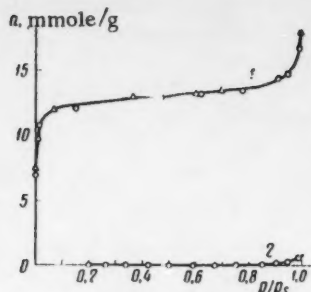
Fig. 1. Sorption isotherms for water vapor at 20° (1) and nitrogen at −195° (2) on MS-4A.
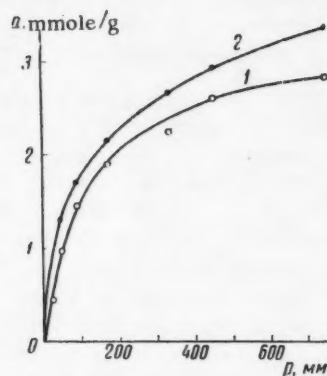


Fig. 2. Adsorption isotherms for nitrogen vapor at −76° on MS-4A. 1) Nonequilibrium experimental isotherm; 2) isotherm calculated from the potential theory of adsorption.
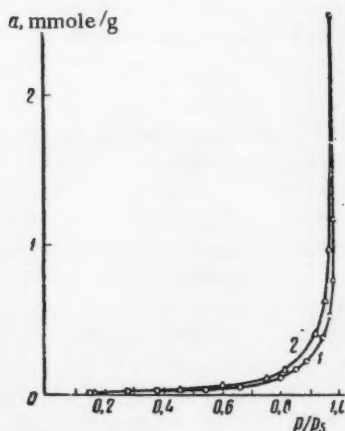


Fig. 3. Isotherms of the sorption (1) and desorption (2) of benzene vapor at 20° on MS-4A.

1. We determined the sorption and, in some cases, desorption isotherms for nitrogen vapor at −195°, and water, benzene, and cyclohexane at 20°. The apparatus used for the investigation was essentially the same as that given in [2]. The adsorbents were first evacuated at 350° until a residual pressure of $1 \cdot 10^{-6}$ mm Hg was reached. Experiments with different vapors were carried out both on the same samples of adsorbents and on fresh samples; their reproducibility, especially for the adsorption branches of the isotherms, was satisfactory.

Figure 1 gives isotherms for the sorption of water and nitrogen vapor on MS-4A. Water molecules readily penetrated through the windows of the elementary spaces of the crystal structure of the zeolite, i.e., into the micropores, and therefore water vapor was adsorbed readily. The isotherm rose steeply in the region of low equilibrium relative pressures and became flatter in the middle region. The final rise in the curve at high relative pressures close to $p/p_s = 1$ was connected with the sorption of water vapor in the secondary porous structure of MS-4A. The adsorption of nitrogen vapor at −195° with the normal wait before the measurement of each experimental point (a few hours) was extremely low up to high relative pressures, where sorption of vapor occurred in the secondary porous structure of MS-4A. However, in this case the low adsorption power of MS-4A was not caused by the impassability of the micropore windows to the nitrogen molecules, but the closeness of the diameter of the windows to the critical size of the nitrogen molecules. As a result, as was shown in [1], the adsorption kinetics were characterized by a considerable activation energy and the adsorption rate became insignificantly low at low temperatures. At the higher temperature of −76°, the nitrogen, which was then in the gaseous state, was adsorbed by MS-4A, though slowly. Curve 1 in Fig. 2 shows the nonequilibrium isotherm obtained for the adsorption of nitrogen on MS-4A at −76°.

The windows of the micropores of MS-4A are impassable to benzene and cyclohexane molecules and these vapors are sorbed only on the outer surface of the microscopic crystals forming the granules and in the gaps between them, i.e., in the secondary porous structure. As an example, Fig. 3 shows isotherms of sorption and desorption of benzene vapor at 20° on MS-4A with a larger scale along the ordinate axis. The branches of the isotherm are concave and at relative pressures above 0.8 there is a sharp rise in the curves, which asymptotically approach the axis $p/p_s = 1$. Equilibrium was reached slowly at $p/p_s = 1$ and in our experiments there was no point in obtaining the true equilibrium values of limiting sorption. The isotherms show the hysteresis loop typical of capillary condensation of benzene vapor. The point at the beginning of the hysteresis corresponds to a relative pressure of ∼0.17, as for active charcoals [3].

The apparent diameters of the windows of the molecular sieve MS-5A are 5.0-5.6 A instead of 4.0-4.75 A for MS-4A. Therefore, MS-5A adsorbed water vapor at 20° and nitrogen at −195° at quite high rates (Fig. 4). Cyclohexane vapor was adsorbed only in the secondary porous structure of MS-5A. Figure 5 shows the adsorption and desorption branches for benzene vapor, which are analogous in form to the branches of the isotherms for MS-4A (Fig. 3). The specific outer surface of the zeolite crystals, was 10.6 $m^2/g$ for MS-5A.

Fig. 4. Isotherms of the sorption of water vapor at 20° (1), nitrogen at −195° (2), and cyclohexane at 20° (3) on MS-5A.



Fig. 5. Isotherms of the sorption (1) and desorption (2) of benzene vapor at 20° on MS-5A.
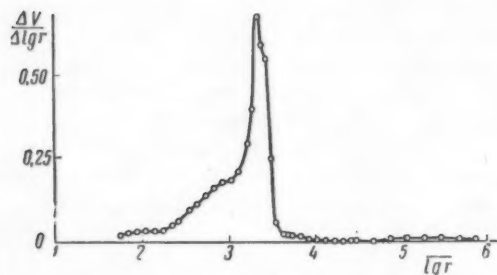


Fig. 6. Differential pore-volume distribution for MS-5A.

2. Low- [4] and high-pressure porosimeters were used for investigating the secondary porous structure of granules of MS-4A and MS-5A by forcing mercury into the pores. The high-pressure instrument was a PM-4 porosimeter, which we remodeled [5]. As an example, Fig. 6 gives a differential pore-volume distribution curve relative to effective radius for MS-5A, corresponding to the equivalent model sorbent with cylindrical pores [6]. A completely analogous curve was obtained for MS-4A.

The differential distribution curve showed a maximum corresponding to an effective pore radius of 2340 A. A considerable portion of the volume of the secondary porous structure filled by mercury, namely, 50%, corresponded to the range of effective pore radii from 1590 to 3550 A. The volume of pores with $r > 3550$ A was very low and did not exceed 0.017 cc/g or 6% of the total volume of mercury forced into the sample at $p = 1500$ atm. The volume of pores with effective radii less than 1590 A represented 42%.

3. For an electron microscope study of the secondary porous structure of zeolites we used the one-step carbon replica method, which is considered to have the best resolving power [7, 8]. Onto the fresh surface of a chip from a zeolite granule was deposited a carbon layer ~150 A thick by thermal atomization in vacuum. The coated side of the sample was pressed against a piece of sticky vinyl insulating tape. After the zeolite had been dissolved in concentrated hydrofluoric acid, a gelatin layer 0.05-0.1 mm thick was formed from an aqueous solution on the washed side of the carbon replica. The sticky layer of vinyl tape was dissolved by immersion in acetone and the gelatin film together with the replica was readily separated. The washed replica on the gelatin backing was then placed on the surface of hot water with the gelatin layer down. The gelatin dissolved and the washed carbon replica was caught with a grid of a sample holder and, after being dried, shadowed with platinum at an angle of 30-40°. This method may be applied to any silicate sorbent and makes it possible to obtain relatively large pieces of undamaged carbon replicas.

Figure 7 gives the most typical of several tens of electron microphotographs, including a stereopair, which were obtained with a UEM-100 electron microscope. There was no appreciable difference in the microphotographs of replicas of MS-4A and MS-5A. Figure 7a gives a low-magnification microphotograph, which gives a general picture of the surface structure of a granule chip. The granules consist of crystals that are sometimes cubic, but largely not of right form from several tenths to several hundredths of a micron in size. A section of this structure is shown at a higher magnification in Fig. 7b. A detailed analysis of a stereophotograph led to the conclusion that the zeolite crystals in the granules are not packed tightly and there are gaps and spaces between them with the same order of size as the fine crystals, i.e., tenths of a micron or several thousand angstroms. Thus, the results of electron microscope and porosimetric studies are in semiquantitative agreement.
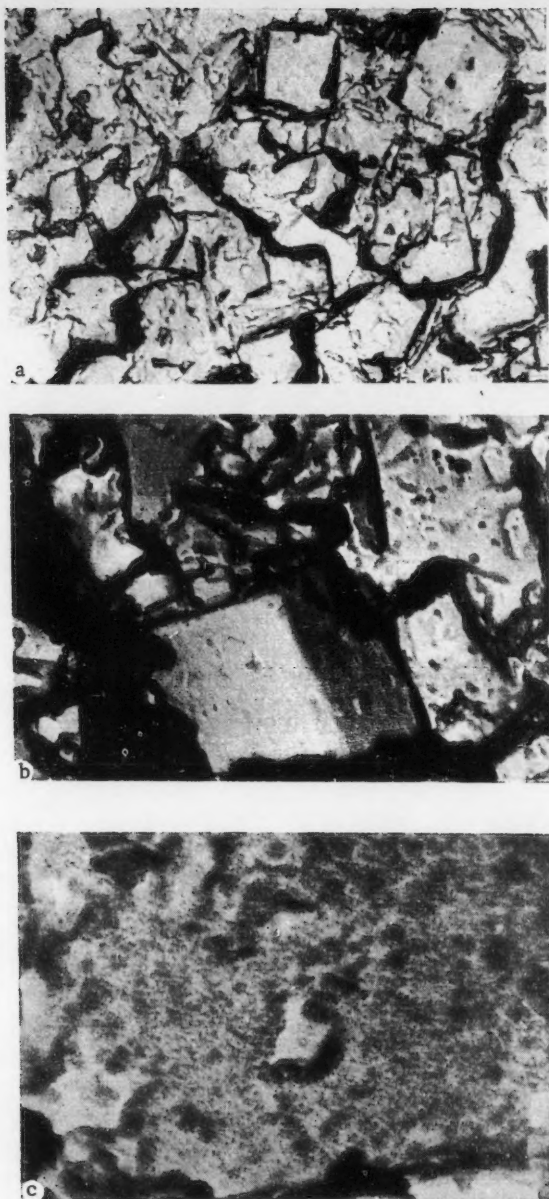
Fig. 7. Electron microphotographs of platinum shaded carbon
replicas of the surface of chips from molecular sieve granules:
a) MS-4A × 6600; b) MS-5A × 31,000; c) MS-44 × 85,000.

At even higher magnifications it was readily seen that the surface of zeolite crystals is not structureless. The microphotographs in Fig. 7b and especially 7c show dark round openings in the crystal faces with diameters of the order of hundredths of a micron, whose origin remains obscure. The microphotograph in Fig. 7c clearly shows the grain structure of the crystal surface, which is reminiscent of the surface structure of chips from coarsely porous silica and aluminosilica gels. There is the possibility that the appearance of this structure is connected with the use of binders in the forming of microscopic zeolite crystals into granules.

## Discussion of Experimental Results

1. The inner elementary spaces in the crystal structure of zeolites, the access to which is limited by the dimensions of the "windows", may be regarded as micropores. In this case zeolites should be regarded as adsorbents of the first structural type, since in the physical adsorption of vapors of nonpolar substances in such fine pores there will be a sharply expressed increase in the adsorption potentials [9, 10]. In [11] we showed that the potential theory of adsorption [12, 9, 13] applies quite satisfactorily to the adsorption of a series of substances on natural and synthetic zeolites.

The isotherm equation for the adsorption of vapors of substances at temperatures not much higher than their boiling points at atmospheric pressure for adsorbents of the first structural type has the following form [9, 13]:

$$a = \frac{W_0}{v} e^{-B\frac{T^2}{\beta^2}(\lg p_s/p)^2}, \tag{1}$$

where $W_0$ is the limiting volume of the adsorption space, coinciding with the volume of the adsorbent micropores, B is an equation constant, depending on the dimensions of the micropores, which have a determining effect on the increase in adsorption potentials, $\beta$ is the affinity coefficient of the characteristic curves, and $\underline{v}$ is the volume of 1 mmole of liquified vapor at the experimental temperature T. In the linear version, Eq. (1) has the form:

$$\lg a = C - D \, (\lg p_s/p)^2, \tag{2}$$

where

$$C = \lg \frac{W_0}{v} = \lg a_0. \tag{3}$$

$$D = 0.434 B \frac{T^2}{\beta^2} \tag{4}$$

The amount of adsorption $a_0$ is the maximum amount of adsorbed vapor, corresponding to space filling of the micropores as a result of merging of the adsorption layers on opposite walls of the micropores. For the standard vapor, in our case nitrogen, $\beta = 1$.
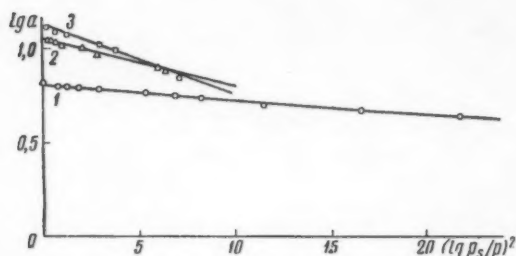


Fig. 8. Adsorption isotherms in the linear form according to Eq. (1): 1) MS-5A, $N_2$, $-195°$; 2) MS-5A, $H_2O$, $20°$; 3) MS-4A, $H_2O$, $20°$.

Figure 8 shows the experimental isotherms for the adsorption of nitrogen vapor on MS-5A at $-195°$ in the linear form according to Eq. (2). The experimental points lie on a straight line quite satisfactorily over a wide range of equilibrium relative pressures, covering four orders of magnitude.

The applicability of the isotherm Eq. (1) to the adsorption of water vapor is an open question. In this case, the electrostatic components of molecular interaction are of considerable importance in addition to the dispersion forces, which are increased in the narrow micropores of zeolites. The reversibility of the adsorption process and the possibility of complete desorption of water vapor by pumping out zeolites at relatively low temperatures, for example, 350°, shows that there is hardly any chemisorption of water vapor. Therefore, it seems to us that there are grounds for estimating the applicability of the potential theory to the adsorption of water vapor on the molecular sieves MS-4A, and MS-5A.

Figure 8 shows isotherms for the adsorption of water vapor at 20° on MS-4A and MS-5A in the linear form according to Eq. (2). In general, the experimental points lie satisfactorily on straight lines. Unfortunately, the adsorption of water vapor in the range of relative pressures of $1 \cdot 10^{-5} - 1 \cdot 10^{-3}$ was not studied as our sorption apparatus lacked special pressure gauges for measuring low equilibrium water vapor pressures ($p/p_s < \cdot 10^{-3}$). Table 1 gives the constants of the adsorption isotherm Eq. (1) and the ranges of relative pressures over which the adsorption isotherm equation agrees with experimental data.

The maximum volumes of the adsorption space of MS-5A determined with nitrogen and water differed by approximately 10%. The value of the constant $B = 2.84 \cdot 10^{-6}$ for nitrogen as the standard vapor corresponds to the

## TABLE 1

Constants of Adsorption Isotherm Equation

| adsorbent | Vapor | $T°,K$ | $a_0,$ mmole/g | $W_0,$ cc/g | $B \cdot 10^6$ | $\beta$ | Range of applicability $p/p_s$ |
|---|---|---|---|---|---|---|---|
| MS-5A | $N_2$ | 78 | 6,31 | 0,219 | 2,84 | 1,00 | $2 \cdot 10^{-5} — 4 \cdot 10^{-1}$ |
| MS-5A | $H_2O$ | 293 | 11,22 | 0,202 | 2,84 | 2,06 | $< 2 \cdot 10^{-3} — 3 \cdot 10^{-1}$ |
| MS-4A | $H_2O$ | 293 | 12,95 | 0,233 | 4,10 | 2,06 | $< 2 \cdot 10^{-3} — 3 \cdot 10^{-1}$ |

## TABLE 2

Comparison of the Calculated and Experimental Values of Adsorption of Water Vapor for Molecular Sieves

| Adsorbent | $a,$ mmole/g | | | | | | |
|---|---|---|---|---|---|---|---|
| | $20°, p/p_s = 5,71 \cdot 10^{-3}$ | | | $80°, p/p_s = 2,82 \cdot 10^{-3}$ | | $80°, p/p_s = 7,05 \cdot 10^{-3}$ | |
| | calc. | our expts. | Kel'tsev's expts. | calc. | Kel'tsev's expts. | calc. | Kel'tsev's expts. |
| MS-4A | 11,7 | 11,8 | 10,6 | — | — | 10,7 | 10,0 |
| MS-5A | 10,3 | 9,9 | 9,4 | 6,2 | 5,6 | 9,7 | 8,9 |

value B = $0.309 \cdot 10^{-6}$ if benzene is taken as the standard vapor (then $\beta = 0.33$ for nitrogen [3]). This level of the constants B corresponds to an adsorbent with extremely fine micropores. For the most finely porous active carbon from polyvinylidene chloride we have $W_0 = 0.475$ cc/g and B = $0.407 \cdot 10^{-6}$. Consequently, the vapor adsorption isotherms for MS-5A rise even more steeply than those for active carbon from polyvinylidene chloride in the initial region of equilibrium relative pressures. The adsorption isotherms of MS-4A differ little in nature from those of the active carbon (B = $0.447 \cdot 10^{-6}$ with benzene as the standard vapor); the maximum volume of the adsorption space for MS-4A is somewhat higher than that for MS-5A.

However, the main criterion of the applicability of the potential theory of adsorption, in addition to agreement between experimental data and the adsorptive isotherm equation, is the fulfillment of the temperature dependence, which would show that the characteristic curve is independent of temperature. As we did not have our own experimental data, we used the results of a determination of the static activity of analogous industrial samples of MS-4A and MS-5A with respect to water vapor at 20 and 80° and equilibrium pressures p = 1 and 25 mm Hg, which were kindly provided by N. V. Kel'tsev. In Table 2 we compare experimental values for the adsorption of water vapor with values calculated from Eq. (1). The constants $W_0$, B, and $\beta$ for water were taken from Table 1 and the values of $p_s$ and v corresponded to tabular values for the bulk liquid phases.

The deviation between the calculated values and those we measured for the adsorption of water vapor did not exceed 3%. All the data of Kel'tsev were low by 7-10% in comparison with the calculated values. It is probable that these deviations are within the limits of permissible differences in the adsorption properties of industrial batches of molecular sieves. On the whole, Eq. (1) expresses the temperature dependence of the adsorption isotherm quite satisfactorily.

According to the potential theory, for the case of adsorption caused only by dispersion forces, the affinity coefficient approximately equals the ratio of the polarizabilities of water and nitrogen, which is 0.83, or the ratios of the parachors of the substances, which is 0.87 (for the parachors calculated by the Bachinskii-Macleod formula). According to the data in Table 1, the experimental affinity coefficient is a factor of approximately 2.5 greater, which directly indicates substantially greater adsorption of vapors by synthetic zeolites. This evidently indicates the relatively small role of true dispersion forces in the adsorption of water vapor on zeolites.

From the constants $W_0$, B, and $\beta$ for MS-4A corresponding to the water vapor adsorption isotherm, it is possible to obtain an idea of the equilibrium adsorption of nitrogen at $-76°$, i.e., at a temperature above the critical point. In Fig. 2, curve 2 shows the equilibrium adsorption calculated from the adsorption isotherm equation for gases (23) given in [13]. The experimental isotherm (curve 1) differs appreciably from the equilibrium.
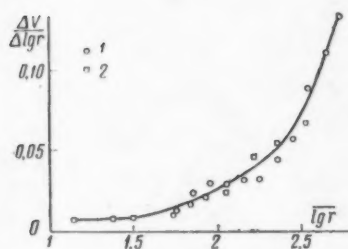


Fig. 9. Section of differential pore-volume distribution curve for MS-5A: 1) forcing mercury into the pores; 2) sorption of benzene vapor.

2. In conclusion, we attempted to obtain a more complete concept of the secondary porous structure of Linde molecular sieves. As an example, Fig. 9 shows a section of the differential pore-volume distribution curve according to the logarithms of the effective radii for MS-5A, on which are superposed the results of sorption and porosimetric measurements. The differential pore volumes were calculated from the desorption branch of the benzene vapor sorption isotherm without the introduction of corrections for the thickness of the adsorption layers, which mainly affected the values of the effective radii. In this case, this difference was concealed because of the logarithmic scale of the radii. On the whole, we have sufficiently close values of the differential pore volumes where the sorption and porosimetric measurements overlap (Fig. 9).

In our experiments, the maximum amount of mercury was forced into the pores at 1500 atm, at which pores with effective radii equal to or greater than 50 A were filled. According to

Kelvin's formula, for benzene at 20°:

$$r = \frac{9,15}{\lg p_s/p} \text{ A} \tag{5}$$

An effective pore radius of 50 A corresponds to an equilibrium relative pressure $p/p_s = 0.65$ in the capillary condensation of benzene vapor. At this pressure, the pores of the adsorbent with effective radii equal to or less than 50 A are filled. As a result, the sums of the sorption volumes of benzene $V_b$ at $r \leq 50$ A and the injected mercury volumes $V_{Hg}$ at $r > 50$ A represent the total volumes of the secondary porous structure of the Linde molecular sieves studied. Table 3 gives the values of $V_b$ and $V_{Hg}$, the volumes of the secondary porous structure $V_2$

$$V_2 = V_b + V_{Hg}, \tag{6}$$

the maximum sorption volumes with respect to benzene $v_s$, and the fraction $v_s/V_2$ of filling of the secondary porous structure by capillary condensation of benzene vapor at practically, but not strictly equilibrium maximum sorption. The point is that the adsorption branches of the benzene vapor sorption isotherms illustrated in Figs. 3 and 5 asymptotically approach the ordinate axis at $p/p_s = 1$ and in this limiting pressure region, the equilibrium is established very slowly.

According to the data in Table 3, the mercury forced in filled 97% of the volume of the secondary porous structure of the molecular sieves, while at practically maximum sorption of benzene vapor, only 76-69% of the volume was filled. The volume of MS-4A that was not filled at maximum sorption of benzene vapor $V_2-v_s = 0.084$ cc/g, according to the integral curve of mercury injection, corresponds to an effective pore radius $r = 2630$ A, which corresponds to $p/p_s = 0.992$ according to formula (5). For MS-5A, $V_2-v_s = 0.111$ cc/g, $r = 2320$ A, and $p/p_s = 0.991$. These relative pressures were undoubtedly realized in our experiments, but as a result of the very low sorption rates, the equilibrium states were not realized during measurements lasting a few hours. In principle, in sufficiently long experiments at $p/p_s = 1$ it would probably be possible to achieve practically complete filling of the secondary porous structure of MS-4A and MS-5A as a result of capillary condensation of benzene vapor.

The primary porous structure of the molecular sieves consists of micropores which are only accessible to molecules of substances capable of penetrating through the windows into the elementary spaces of the crystal structure, i.e., properly into the micropores. The maximum volumes of the adsorption space $W_0$ in this case represent the volume of the micropores or the volume of the primary porous structure $V_1 = W_0$. The sum of the volume $V_\epsilon$

$$V_\varepsilon = V_1 + V_2 \tag{7}$$

## TABLE 3

Data on Volumes of Secondary Porous Structure of Linde Molecular Sieves

| Adsorbent | $V_b$, cc/g at $r < 50$ A | $V_{Hg}$, cc/g at $r > 50$ A | $V_2$, cc/g | $v_s$, cc/g | $\dfrac{V_{Hg}}{V_2}$ | $\dfrac{v_s}{V_2}$ |
|---|---|---|---|---|---|---|
| MS-4A | 0,007 | 0,295 | 0,302 | 0,218 | 0,985 | 0,722 |
| MS-5A | 0,009 | 0,214 | 0,323 | 0,212 | 0,972 | 0,656 |

## TABLE 4

Pore Volumes of Granules of Linde Molecular Sieves

| Adsorbent | $W_0$, cc/g $N_2$ | $W_0$, cc/g $H_2O$ | $V_1 = \overline{W}_0$, cc/g | $V_2$, cc/g | $V_e$, cc/g |
|---|---|---|---|---|---|
| MS-4A | — | 0,233 | 0,233 | 0,302 | 0,535 |
| MS-5A | 0,219 | 0,202 | 0,210 | 0,323 | 0,533 |

gives the sum of the pore volumes of the synthetic zeolite. Table 4 gives the over-all characteristics of the porous structure of the samples of Linde molecular sieves studied.

## SUMMARY

1. The adsorption properties of granulated industrial samples of Linde molecular sieves 4A and 5A with respect to the vapors of substances whose molecules penetrate through the windows into the elementary spaces of the zeolite crystals are described satisfactorily by the potential theory of adsorption.

2. The secondary porous structure of the granules, which is formed by gaps and spaces between touching zeolite crystals, could be described quantitatively by sorption and mercury porosimetric methods.

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# PROPERTIES OF SURFACE SOLUTIONS AND SURFACE HETEROGENEITY

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Adsorption layers formed on the surface of a solid during adsorption of mixtures of gases or vapors may be regarded as surface solutions. Even on an ideal homogeneous surface, the properties of such surface solutions will not be the same as those of the corresponding three-dimensional solutions of the same substances. With a change to real adsorbents with a heterogeneous surface, the very conception of a surface solution becomes conditional to a considerable extent. In this case there is no homogeneous surface phase with the same properties on any part of the adsorbent surface as the composition of the surface solution varies from point to point in accordance with the distribution function of the adsorption potentials on sections of the surface, and the "composition of the surface solution" determined experimentally in the mean value for the whole surface. Nonetheless, as will be shown below, the determination of the properties of such surface solutions is of definite interest as certain peculiarities associated with the heterogeneity of the surface are found in this way.

Let us first use Langmuir's theory to examine the adsorption of two substances on an energetically homogeneous surface with no interaction between the adsorbed molecules. As is known, the adsorption of each component in this case is expressed by the equations

$$a_1 = a_m b_1 p_1 / (1 + b_1 p_1 + b_2 p_2), \quad a_2 = a_m b_2 p_2 / (1 + b_1 p_1 + b_2 p_2), \tag{1}$$

where $p_1$ and $p_2$ are the partial pressures in the gas phase, $a_1$ and $a_2$ are the amounts of adsorption of the components, $b_1$ and $b_2$ are the adsorption coefficients, and $a_m$ is the limiting amount of adsorption or the total number of adsorption centers.

Let us take $a_1$ and $a_2$ as independent variables and determine the relation of the pressure $p_1$ and $p_2$ to the composition of the adsorption phase along the total adsorption isostere, i.e., when $a_{12} = a_1 + a_2 = $ const.

By solving Eq. (1) for $p_1$ and $p_2$, we find:

$$p_1 = a_1/b_1 (a_m - a_1 - a_2), \quad p_2 = a_2/b_2 (a_m - a_1 - a_2). \tag{2}$$

At the same time, when $a_2 = 0$, and, correspondingly, when $a_1 = 0$

$$p_1^0 = a_1^0/b_1 (a_m - a_1^0), \quad p_2^0 = a_2^0/b_2 (a_m - a_2^0), \tag{3}$$

where the superscript zero denotes values referring to the individual adsorption isotherms.

When $a_{12} = a_1^0 = a_2^0 = $ const, from Eqs. (2) and (3) we obtain:

$$p_1 = \frac{a_1}{a_{12}} p_1^0 = N_{\sigma_1} p_1^0, \quad p_2 = \frac{a_2}{a_{12}} p_2^0 = N_{\sigma_2} p_2^0, \tag{4}$$

where $N_\sigma$ is the mole fraction of the component in the adsorption phase.

Equation (4) is evidently the expression for Raoult's law for the adsorption phase and the values $p_1^0$ and $p_2^0$ may be regarded as a type of "saturated vapor pressure" of the two substances for the given isostere $a_{12} = $ const. On this basis we can state that along the total adsorption isostere the adsorption phase behaves as a two-dimensional ideal solution. This statement applies only in the cross sections $a_{12} = $ const since in all other possible cross sections of the thermodynamic surfaces of adsorption, Eq. (4) does not hold.

We will consider the adsorption system as ideal if Eq. (4) holds along the total adsorption isostere, in contrast to real adsorption systems, for which deviations in the properties of surface solutions from Raoult's law are observed.

We should note that an adsorption system described by Langmuir's Eq. (1) is not the only possible example of an ideal adsorption system.

If the adsorption phase is a two-dimensional ideal solution, then it is readily shown that the total adsorption isosteres are linear. In actual fact, as $N_{\sigma_1} + N_{\sigma_2} = 1$, from Eq. (4) we obtain

$$p_1/p_1^0 + p_2/p_2^0 = 1, \qquad (5)$$

i.e., the equation of a linear isostere $a_{12}$ = const in the coordinates $p_1$ and $p_2$.

At first glance it may seem that the reverse statement is also true, namely, that the adsorption phase is ideal if the isostere of $a_{12}$ is linear. However, in the general case this statement is untrue. Let us assume that the isostere of $a_{12}$ is linear, i.e., Eq. (5) holds. In the general case, by introducing the "activity coefficients" $f_1$ and $f_2$ for the components of the adsorption phase in analogy with three-dimensional solutions, we may write

$$p_1 = N_{\sigma_1} f_1 p_1^0, \quad p_2 = N_{\sigma_2} f_2 p_2^0, \qquad (6)$$

for which it follows:

$$p_1/p_1^0 + p_2/p_2^0 = N_{\sigma_1} f_1 + N_{\sigma_2} f_2 = 1. \qquad (7)$$

It is evident that for an ideal solution $f_1 = f_2 = 1$ and Eq. (7) coincides with Eq. (5). However, in the general case it cannot be concluded from Eq. (7) that both coefficients $f$ equal unity, i.e., to state that the adsorption phase is ideal.

Equation (7), which gives a relation between $f_1$ and $f_2$ with the condition (5), may be rewritten in the following form:

$$f_1 = 1 + \frac{N_{\sigma_2}}{N_{\sigma_1}} (1 - f_2), \qquad (8)$$

which indicates that the coefficients $f_1$ and $f_2$ cannot be simultaneously greater than unity or simultaneously less than unity. If $f_2 < 1$ then the second term in the right-hand part of this expression is positive when $0 \leq N_{\sigma_2} \leq 1$ and therefore over this range $f_1 > 1$. In other words, if the total adsorption isostere is linear, then with this condition the activity coefficient of one component of the surface solution $f_1 > 1$ and that of the other $f_2 < 1$, i.e., the deviations from Raoult's law for one component of the surface solution are positive, while those for the other component must be negative.



Fig. 1. Phase diagram of surface solutions for the system $C_2H_4-C_2H_6-$ carbon at 25°; $a_{12} = 1.2$ mmole/g.

As was shown previously [1], the total adsorption isostere is very nearly linear for the adsorption of gas mixtures in the systems we studied. On the basis of what has been stated, it is clear that the coefficients $f_1$ and $f_2$ should show the given peculiarity for such systems. As an illustration, we give in Fig. 1 a "phase diagram of surface solutions" for the adsorption system ethylene—propylene—carbon [1] at 25°. In this diagram, the mole fraction $N_{\sigma_2}$ of the more rapidly adsorbed component (propylene in the given case) in the adsorption phase is plotted along the abscissa axis, and the "relative pressures" $p_1/p_1^0$ and $p_2/p_2^0$ of ethylene and propylene over the surface solution along the isostere $a_{12} = 1$. mmole/g are plotted along the ordinate axis. This phase diagram was constructed from interpolated experimental data. For any composition $N_{\sigma_2}$, which is marked by the letter C on Fig. 1, the coefficient $f_2$ equals the ratio $F_2C : I_2C$ while the coefficient $f_1$ equals the ratio $F_1C : I_1C$. Over the whole range of changes in $N_{\sigma_2}$, the curve $A_1B_2$ for the component adsorbed most, propylene, lies <u>below</u> the diagonal line $p_2/p_2^0 = N_\sigma$ which expresses Raoult's law for the ideal surface solution, while the curve $A_2B_1$ for the component adsorbed least, ethylene, lies completely <u>above</u> the corresponding line $p_1/p_1^0 = N_{\sigma_2}$.

Phase diagrams constructed for other isosteres of $a_{12}$ of this system have a similar form. We obtained qualitatively identical phase diagrams on examining the adsorption equilibrium in the following systems: carbon dioxide—ethylene—carbon at 25° [2], ethylene—propylene—carbon at 7° [1], acetone—chloroform—silica gel at 35° [3], and oxygen—nitrogen—anatase at −195° [4]. As is known, the deviations from Raoult's law for three-dimensional solutions generally have the same sign for both components of a binary solution. At a given solution composition, these deviations are either both positive ($f_1 > 1$ and $f_2 > 1$) or both negative ($f_1 < 1$ and $f_2 < 1$). In this sense the

behavior of surface solutions is a special case as the signs of the deviations from Raoult's law are not the same for the two substances. These deviations are negative ($f_2 < 1$) for the component adsorbed most, and positive ($f_1 > 1$) for the component adsorbed least. Below we will attempt to present arguments in favor of the concept that this anomaly in the properties of surface solutions is an essential consequence of energetic heterogeneity of the adsorbent surface. The solution of this problem in the general form apparently presents insuperable mathematical difficulties and there-fore we will limit ourselves to the examination of a particular case.

Let us assume that the surface of the adsorbent is heterogeneous and that on each homogeneous section the adsorption of the gas mixture proceeds in accordance with Langmuir's theory. Let us start from the most probable assumption that the local values of the heats of adsorption of the two components on any homogeneous section of the surface are proportional to each other [5], i.e.,

$$Q_2 = \varepsilon Q_1, \tag{9}$$

where the coefficient $\varepsilon$ is the same for all sections. Since

$$b_2 = b_{02} e^{Q_2/RT} \text{ and } b_1 = b_{01} e^{Q_1/RT}, \tag{10}$$

then the relation between $b_2$ and $b_1$ is determined by the expression

$$b_2 = c b_1^{\varepsilon}. \tag{11}$$

| No. of section, $i$ | $a_{mi}$ | $b_{1i}$ | $b_{2i}$ |
|---|---|---|---|
| 1 | 0,3 | 10 | 100 |
| 2 | 0,3 | 5 | 35,5 |
| 3 | 0,9 | 1 | 3,18 |
| 4 | 1,5 | 0,5 | 1,12 |

Let us define the heterogeneous surface by the table, which gives values of $a_{mi}$, $b_{1i}$, and $b_2$ for each of the four sections $i$ with the adsorption coef-ficients $b_{2i}$ calculated from the Eq. (11) with $c = 100$ and $\varepsilon = 1.5$, while the total number of adsorption centers over the whole surface $a_m = 3$ mmole/g. It is evident that on such a surface the adsorption of each component at the pressures $p_1$ and $p_2$ may be given by the equations

$$a_1 = \sum_{i=1}^{4} \frac{a_{mi} b_{1i} p_1}{1 + b_{1i} p_1 + b_{2i} p_2}; \quad a_2 = \sum_{i=1}^{4} \frac{a_{mi} b_{2i} p_2}{1 + b_{1i} p_1 + b_{2i} p_2}, \quad a_{12} = a_1 + a_2.$$

Hence one can readily obtain the equations of individual isotherms for adsorption of the first (A) and (B) gases at $p_2 = 0$ and $p_1 = 0$, respectively. We should note that the values given in the table were chosen in such a way that the individual adsorption isotherm for gas A calculated from the equations (12) almost completely coincides with the isotherm for adsorption of $CO_2$ on AG-2 carbon [2], while the calculated individual isotherm for B lies appreciably above the corresponding isotherm for $C_2H_4$ on the same carbon.

If we substitute $a_{12} = \text{const} = 1$ mmole/g in the Eq. (12) we obtain an expression for the total adsorption isostere, giving the relation of $p_2$ to $p_1$. Even in the particular case examined, the expression obtained does not make it possible to find $p_2$ as an explicit function of $p_1$. However, by taking a series of values of $p_1$, we can find the cor-responding values of $p_2$ by selection and thus obtain an idea of the form of the total adsorption isostere for $a_{12} = 1$.

In the lower part of Fig. 2, the line AB, passing through the points A and B with the coordinates $p_1^0 = 450$, $p_2^0 = 0$) and ($p_1^0 = 0$, $p_2^0 = 134$), which correspond to the values of $p_1^0$ and $p_2^0$ on the individual isotherms for the adsorption of gases A and B at $a_1^0 = a_2^0 = 1$, is the total adsorption isostere for $a_{12} = 1$ for an ideal system [see Eq. (5)]. The points of the isostere for $a_{12} = 1$ of a heterogeneous surface, calculated by the Eqs. (12), are represented by circles which lie somewhat below this line. As Fig. 2 shows, the isostere for $a_{12} = 1$ for a heterogeneous surface is a slightly concave curve, passing through the points A and B. In the case examined, the deviations of this isostere from the line AB are small and therefore, in the first approximation we can regard the total adsorption isostere for $a_{12} = 1$ for the given heterogeneous surface as linear without particular error.

Analogous calculations for a series of other examples led to the conclusion that in the general case of adsorption of mixtures of gases in accordance with Langmuir's equation, the isostere of total adsorption on a heterogeneous surface is a concave curve, which deviates from the linear isostere to a greater or lesser extent. These deviations depend on

the form of the distribution function of the adsorption coefficients with respect to the surface sections, and apparently increase with an increase in $\epsilon$. However, they are small as a rule so that the isosteres for $a_{12}$ = const may be approximated by straight lines especially when $1 < \epsilon < 1.5$.

A comparison of the most characteristic cross sections of thermodynamic surfaces given by the Eqs. (12) with the corresponding cross sections for real systems reveals great similarity in all cases, as is shown well by Fig. 2. The lower part of Fig. 2, shows isosteres for $a_{12} = a_1 = a_2 = 0.5$ and $a_{12} = 1$, calculated for the mixture of gases A + B by the Eqs. (12) and the upper part of Fig. 2 shows the corresponding isosteres for the system $CO_2 + C_2H_4$ + carbon [2]. If, for example, for $a_1 = 0.5$ mmole/g we calculate for a series of values of $p_1$ the corresponding values of $p_2$ from the first of the Eqs. (12), then we obtain a concave isostere for $a_1 = 0.5$, which is almost completely the same as the isostere for $a_1 = 0.5$, for the mixtures $CO_2 + C_2H_4$. At the same time, the isostere for $a_2 = 0.5$, calculated from the second Eq. (12), is practically a straight line in complete agreement with the experimental isostere for $a_2 = 0.5$ for the mixture $CO_2 + C_2H_4$. Thus, in the adsorption of a mixture of two gases in accordance with Langmuir's equation on a heterogeneous surface, the isosteres for $a_1$ = const in the coordinates ($p_1$, $p_2$) give a family of concave curves (like the isosteres of $CO_2$), while the isosteres for $a_2$ = const form a family of straight lines, corresponding to the isosteres for ethylene in the system $CO_2-C_2H_2-AG$ -2 carbon.
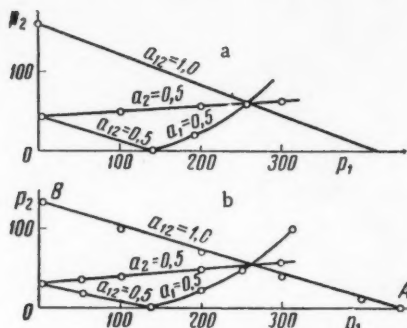


Fig. 2. Comparison of adsorption isosteres for the system: a) $CO_2-C_2H_4-$carbon; b) A$-$B$-$heterogeneous surface.



Fig. 3. Phase diagram of surface solutions with Langmuir adsorption of mixtures of the gases A + B on a heterogeneous surface.

If we now calculate the values of $a_1$ and $a_2$ from the equations (12) for the values of $p_1$ and $p_2$ found at a series of points on the isostere for $a_{12} = 1$ and find the mole fractions $N_{\sigma_2}$ for the points, it is possible to construct a "phase diagram of the surface solutions," i.e., curves of $p_1 = \varphi_1(N_{\sigma_1})$ and $p_2 = \varphi_2(N_{\sigma_2})$. The result of these calculations is shown in Fig. 3 in the coordinates $N\sigma_2$, $p/p^0$. The curves of $\varphi_1$ and $\varphi_2$ in Fig. 3 are very similar to the corresponding curves in Fig. 1. Over its whole length the curve of $\varphi_1$ lies above the diagonal line (positive deviations from Raoult's law) while the curve of $\varphi_2$ lies below the corresponding diagonal line (negative deviations from Raoult's law) and this means that over the whole range of changes in $N\sigma_2$, the "activity coefficient" for the less adsorbed component A, $f_1 > 1$, while this coefficient for the more adsorbed component B, $f_2 < 1$. In the construction of Fig. 3, it was assumed that the isostere for $a_{12} = 1$ is strictly linear. Allowance for the actual nonlinearity of the isostere changes the two curves only very little and makes them slightly unsymmetrical.

On the basis of this we can consider it extremely probable that in the adsorption of a mixture of two gases on a heterogeneous surface and with condition (9), the inequalities $f_1 > 1$ and $f_1 < 1$ must hold. The anomaly of the activity coefficients in this case is caused solely by the heterogeneity of the surface. Although this conclusion was drawn by examining a particular case, there are grounds for considering that it is general as similar calculations for other examples of a heterogeneous surface lead to a qualitatively identical result.

As is well-known, in the simplest case of the Langmuir theory, formulated by Eqs. (1) and (12), no allowance is made for interaction forces between the adsorbed molecules. The question naturally arises as to how these interaction forces will affect the phase diagrams of surface solutions on a homogeneous surface, the form of the total
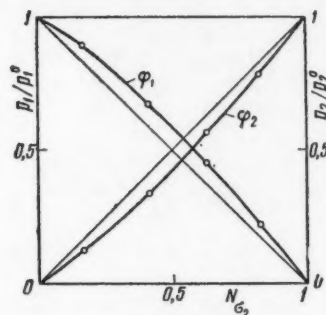
adsorption isostere, and the coefficients $f_1$ and $f_2$ for adsorption on a heterogeneous surface.

To solve this problem let us first draw a certain analogy between a two-component adsorption phase on a homogeneous surface and a normal three-dimensional binary solution. First of all it is evident that from the point of view of the phase rule, this analogy has meaning only if we examine the adsorption phase with the condition that $a_{12} =$ const, i.e., along the total adsorption isostere. In this case and at constant temperature, the pressures $p_1$ and $p_2$ of the two components over the adsorption phase are unequivocally determined by the composition of this phase exactly as in the case of a normal solution.

Let us examine the three simplest types of normal solution: a) ideal, b) nonideal with negative deviations from Raoult's law ($f_1 < 1$ and $f_2 < 1$), and c) nonideal with positive deviations from Raoult's law ($f_1 > 1$ and $f_2 > 1$).
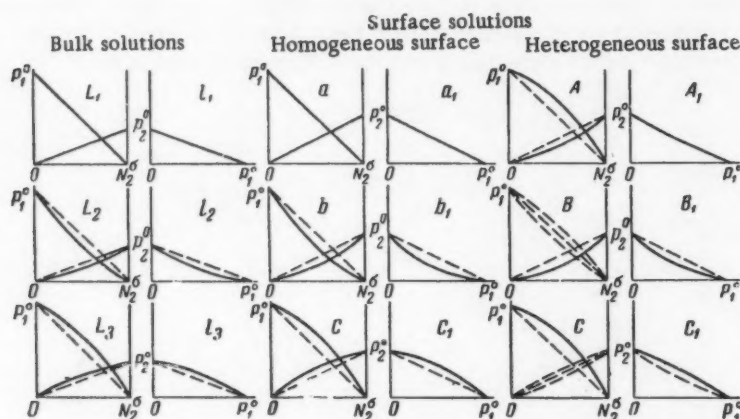


Fig. 4. Comparison of the properties of bulk and surface solutions.

Figure 4 shows phase diagrams of these solutions, which are denoted by the letters $L_1$, $L_2$, and $L_3$, respectively. For each of these solutions we can construct its particular type of "isostere", if we plot in the two coordinate axes $p_1$ and $p_2$, the connected values of the equilibrium pressures $p_1$ and $p_2$ of the two components over the solution, referring to each given solution composition. These "isosteres" for the solution are denoted by the letters $l_1$, $l_2$, and $l_3$ in Fig. 4. It is readily shown that the isostere $l_1$ for an ideal solution is a straight line, giving intercepts on the axes $p_1^0$ and $p_2^0$, which equal the saturated vapor pressures of the pure components. For the solution $L_2$ with negative deviations from Raoult's law, the corresponding isostere $l_2$ is a concave curve, and for the solution $L_3$ with positive deviations, the isostere is expressed by a convex curve.

Negative deviations correspond to a greater interaction between molecules of the two types A and B in comparison with the interactions of A and A or B and B. It may be considered conditionally that this case represents the appearance of attraction forces in the solution. Similarly, positive deviations from Raoult's law correspond to lower interaction between A and B in comparison with the interactions of A and A or B and B. It may be considered conditionally that this case represents the appearance of repulsion forces. Under these conditions it may be stated that the presence of "attraction forces" between the molecules A and B in solution leads to a concave isostere, while the presence of "repulsion forces" is characterized by a convex isostere. There is no interaction for an ideal solution (or the interaction between A and B equals the corresponding interactions between A and A or between B and B) and in accordance with this, the isostere is linear.

From our point of view, there are grounds for thinking that in adsorption on a homogeneous surface there are three possible analogous simplest types of surface solution, which are denoted by the letters a, b, and c in Fig. 4.

First type (Fig. 4, a and a$_1$). An ideal surface solution obeying Raoult's law. In this case, adsorption is described by Langmuir's equations (or Henry's equations) and therefore the total adsorption isostere (Fig. 4, a$_1$) is linear. There is no interaction between the adsorbed molecules.

Second type (Fig. 4, b and $b_1$). Nonideal surface solution characterized by negative deviations from Raoult's law. In this case, adsorption is not described by Langmuir's equations (1). For the two components there are the inequalities $f_1 < 1$ and $f_2 < 1$, caused by the appearance of attraction forces between molecules in the surface layer. As a result of this, the total adsorption isostere (Fig. 4, $b_1$) is concave.

Third type (Fig. 4, c and $c_1$). Nonideal surface solution characterized by positive deviations from Raoult's law ($f_1 > 1$ and $f_2 > 1$), caused by the action of repulsion forces between adsorbed molecules. In this case, adsorption is not described by the equations (1). The total adsorption isostere is convex (Fig. 4, $c_1$).

Of the three given types of surface solution on a homogeneous surface, only the first type has a theoretical foundation as it is a consequence of Langmuir's theory. The following qualitative arguments may be put forward in support of the two remaining types. If for an ideal two-dimensional solution, the total adsorption $a_{12}$ is reached at certain values of $p_1$ and $p_2$, then when there are attraction forces between the molecules in the surface layer, the same value of $a_{12}$ at the same composition of the surface phase $N_{\sigma 2}$ evidently can be obtained at lower values of $p_1$ and $p_2$ due to the appearance of an additional adsorption potential caused by the attraction forces. Thus, this factor must produce deformation of the total adsorption isostere in accordance with the curve $b_1$ in Fig. 4. Similarly, repulsion forces, which decrease the adsorption potential, must lead to an increase in the pressures $p_1$ and $p_2$ at which the previous value of $a_{12}$ is reached at a given composition $N_{\sigma 2}$ and, consequently, must distort the isostere in accordance with $c_1$ in Fig. 4.

Thus, we are correct in expecting that on a homogeneous surface, the properties of the surface solutions will be "normal" in the sense that the deviations from Raoult's law for the two components will have the same sign. The presence of attraction forces between adsorbed molecules should simultaneously reduce the equilibrium pressures of both components over the adsorption phase in comparison with the corresponding equilibrium pressures over an ideal surface solution, while repulsion forces should lead to an increase in the pressure of the components over a nonideal surface solution in comparison with the pressure over an ideal solution of the same composition.

Let us now try to visualize the appearance of phase diagrams of surface solutions and isosteres for $a_{12}$ = const for adsorption on a surface with allowance for interaction forces. As was shown above, with Langmuir adsorption on a heterogeneous surface without interaction, the total adsorption isostere is a slightly concave curve, which differs little from the linear isostere for an ideal system (see Fig. 4, $A_1$). The curve $p_1 = \varphi_1(N_{\sigma 2})$ in Fig. 4, A is convex ($f_1 > 1$), while the corresponding curve $p_2 = \varphi_2(N_{\sigma 2})$ is concave ($f_2 < 1$). In this case, the coefficients $f_1$ and $f_2$ characterize the heterogeneous surface. With attraction forces between molecules in the surface layer we can expect that the phase diagram of the surface solution will have the form shown in Fig. 4, B. The curve $\varphi_2$ for the component adsorbed most in this case must be concave as the superposition of effects produced by attraction forces onto Langmuir adsorption on a heterogeneous surface can only increase the curvature of the curve of $\varphi_2$. At the same time, the curve of $\varphi_1$ may be either convex or concave, depending on the nature of the heterogeneity of the surface. In this case, the total adsorption isostere must be concave as is shown in Fig. 4, $B_1$. Finally, with the presence of repulsion forces in the surface layer (produced, for example, by the interaction of identically oriented dipoles) one can expect that the isostere for $a_{12}$ will be less concave than in case $A_1$, i.e., more linear than in the absence of interaction, and may even be convex, as is shown in Fig. 4, $C_1$. The curve $p_1 = \varphi_1(N_{\sigma 2})$ must be convex (see Fig. 4, C), as repulsion forces must produce a further increase in the positive deviations from Raoult's law for the component adsorbed least, caused by the heterogeneity of the surface. At the same time, the curve of $\varphi_2$ will be either convex or concave, depending on the nature of the heterogeneity and the degree of interaction.

In conclusion, we would like to emphasize one essentially new result which follows from this examination of the properties of surface solutions. As is known, in the investigation of adsorption of one substance on a heterogeneous surface of a real adsorbent, it is not possible to distinguish unequivocally between the effect on adsorption of the true heterogeneity of the surface (i.e., some distribution of the adsorption coefficients with respect to sections of the surface) and the effect of repulsion forces between adsorbed molecules. On the basis of an investigation of the adsorption of gas mixtures, in the given case we can reliably detect heterogeneity of the surface from the form of the curves of $\varphi$ and draw more or less probable conclusions on the existence or absence of interaction forces between the molecules in the surface layer from the form of the total adsorption isosteres.

## SUMMARY

1. In the adsorption of a mixture of two substances in accordance with Langmuir's equation on a homogeneous surface, the adsorption phase behaves as an ideal two-dimensional solution obeying Raoult's law.

2. In contrast to two-component nonideal three-dimensional solutions, for which deviations from Raoult's law for the two components are either simultaneously positive or simultaneously negative, for adsorption solutions on the surface of a solid with the total adsorption isostere linear, these deviations are negative for the component adsorbed most and positive for the component adsorbed least.

3. Calculations for a particular case show that this anomaly in the properties of surface solutions is caused by the heterogeneity of the surface, and the deviations from Raoult's law characterize this heterogeneity rather than the properties of the surface solution.

4. An examination was made of the possible effect of interaction forces between adsorbed molecules on phase diagrams of surface solutions and the form of total adsorption isosteres.

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# "THE PENTOXIDES OF NIOBIUM AND TANTALUM
# AS DEHYDRATION CATALYSTS"

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In an investigation carried out before [1], in which the catalytic properties of the oxides of vanadium, niobium, and tantalum were compared, it was established that niobium pentoxide and tantalum pentoxide exert mainly a dehydrating effect with reference to alcohols: isopropyl alcohol was only dehydrated, while n-propyl alcohol at 400° was dehydrated to the extent of 88% and dehydrogenated to the extent of 3%. In the latter case the gases contained up to 5-10% of saturated hydrocarbons and also CO, indicating that decomposition processes took place simultaneously.

Development of a scientific basis for the selection of catalysts requires a knowledge of the energies by which the reacting atoms are bound to the catalyst. To determine the corresponding energies of the kinetic method [2] based on the multiplet theory, one must investigate the kinetics of a number of individual reactions taking place on the catalysts in question, because a knowledge of the energies of activation of these reactions is required for the calculation involved. Determination of the activation energies of reactions taking place on the pentoxides of niobium and tantalum is also of independent interest from the scientific standpoint, because these catalysts have been little investigated.

From this point of view, we undertook an investigation of the kinetics of the dehydrogenation of isopropyl alcohol on the pentoxides of niobium and tantalum. Isopropyl alcohol was selected because its dehydrogenation takes place without side processes (see above): this is of great advantage for the calculation of activation energies. Because both niobium pentoxide and tantalum pentoxide occur in different modifications which may exhibit different catalytic properties, the oxide samples used were subjected to X-ray phase analysis in addition to an investigation of their catalytic activity.

Niobium pentoxide. The kinetics of the dehydration of isopropyl alcohol were investigated primarily by using a sample of $Nb_2O_5$ (sample 1) that was prepared by oxidizing metallic niobium in the form of finely cut platelets in a muffle furnace at 730-750° for 4-5 hours, which was the time required for the complete conversion of all of the metal into oxide powder. The experiments were carried out in a continuous flow installation developed at our laboratory [3] for the investigation of catalysts. They were conducted in the temperature range of 360-400° at a flow rate of the alcohol amounting to 0.15 ml/min. The volume of the loosely packed catalyst was 2 ml, the volume velocity of the alcohol 4.5 hours$^{-1}$. During the conversion there was evolution of gas at a uniform rate; analysis of the gas showed that it consisted of propylene to the extent of 99-99.5%. The volume of the gas evolved was measured every minute starting with the 9-10th minute after the beginning of the experiment, when the conditions of the system became stationary. The duration of the experiments was 25-30 minutes. The gas volumes were brought to standard conditions of temperature and pressure.

The initial activity of the catalyst was checked systematically (almost after every experiment) by carrying out a control experiment at the initial temperature (360° in most cases). Depending on the temperature of the conversion, the activity of the catalyst began to decrease after it had been used for 30-50 minutes. When its activity had decreased, the catalyst was regenerated by exposing it to a stream of air at 400-410° for 2-3 hours. It was found that the catalyst could be regenerated relatively easily with air; all experiments and a great number of tests for checking the initial activity were carried out with a single portion of the catalyst. It was found that with an increased time of application of the catalyst (including periodic regeneration in an air stream for 2-3 hours) the length of time required for regeneration of the catalyst to its initial activity increased to 6-7 hours. After the
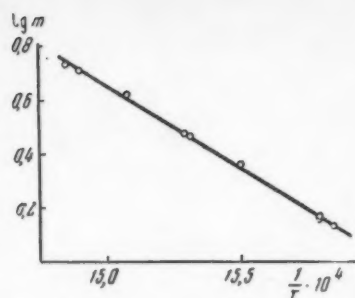
Fig. 1. Dehydration of isopropyl alcohol on $Nb_2O_5$ (sample 1). Relation between lg m and $1/T$.

catalyst had been used for 8 hours, it lost its activity, and the latter could not be restored even by treatment with air for more than 10 hours. However, glowing of a used up sample like this in a muffle furnace at 700° for 2 hours resulted in a restoration of the initial activity of the catalyst; the time of its operation with constant activity without regeneration even increased after this to 80 min. However, subsequent to that, after approximately 90 minutes of operation, the activity dropped by one half and could then not be restored fully either by regeneration in a stream of air or by glowing in a muffle furnace.

An X-ray phase analysis of fresh and spent $Nb_2O_5$ catalysts below) showed that the structure of the crystal lattice of both samples was the same. Thus, during the operation of the catalyst only surface changes take place which do not affect the volume phase, but bring about changes in the activity of the catalyst. According to the data of the X-ray phase analysis, we encounter here a low-temperature $\gamma$-modification of $Nb_2O_5$.

The results obtained in the experiments are given in Table 1 and Fig. 1. The numbers of the experiments in Table 1 correspond to the order in which these experiments were carried out. It follows from the data in Table 1 that the maximum degree of conversion of the alcohol was 12.3%; thus, the experiments were conducted in a range far removed from equilibrium. Under the circumstances, the assumption was justified that the velocity constant k of the reaction was equal to the quantity of gas m evolved per minute (see more about this in ref. [4]).

TABLE 1

Dehydration of Isopropyl Alcohol on $Nb_2O_5$ (sample 1) (flow rate of the alcohol 0.15 ml/min; volume of the loosely packed catalyst 2 ml; at a 100% conversion, m = 43.9 ml/min; $\epsilon$ = 27000 cal/M)

| No. of the experiment | Temp. of the experiment, °C | m(obs.), ml/min per 1ml. of catalyst, brought to STP | lg $k_0$ | m calculated from $\epsilon$ and the mean value of lg $k_0$ | $\dfrac{\epsilon}{\lg k_0} \cdot 10^{-4}$ |
|---|---|---|---|---|---|
| 8 | 358 | 0,68 | 9,192 | 0,70 | 2,94 |
| 12 | 360 | 0,75 | 9,205 | 0,75 | 2,93 |
| 17 | 360 | 0,75 | 9,205 | 0,75 | 2,93 |
| 27 | 360 | 0,73 | 9,193 | 0,75 | 2,94 |
| 25 | 372 | 1,15 | 9,210 | 1,14 | 2,93 |
| 9 | 380 | 1,47 | 9,217 | 1,43 | 2,93 |
| 26 | 381 | 1,50 | 9,206 | 1,50 | 2,93 |
| 13 | 390 | 2,10 | 9,232 | 1,98 | 2,92 |
| 29 | 398 | 2,58 | 9,212 | 2,55 | 2,93 |
| 2 | 400 | 2,70 | 9,201 | 2,70 | 2,93 |
| 5 | 400 | 2,70 | 9,201 | 2,70 | 2,93 |
| | Mean value | | 9,206 | | |

In the experiments with $Nb_2O_5$ close conformity with the Arrhenius equation was observed; all values of lg m fitted onto a straight line when they were plotted as a function of $1/T$ (cf. Fig. 1). Table 1 also lists values of the logarithm of the activity constant (lg $k_0$) calculated for the corresponding values of the activation energy $\epsilon$. It can be seen that the values of lg $k_0$ are sufficiently constant; the values of m calculated from the found values of $\epsilon$ and the mean values of lg $k_0$ (column 5) are in good agreement with the observed values of m (column 3). The ratio of $\epsilon / \lg k_0$ remains constant, which indicates that a logarithmic relation is valid (the so-called compensation effect); the value of the ratio is 2.93. This value is very close to 3, which is characteristic for doublet reactions taking place on oxide catalysts. Further investigation showed that the activity of $Nb_2O_5$ prepared by oxidizing the metal in a muffle furnace depended strongly on the temperature at which the metal was oxidized and the length of time during which the oxide that had formed was heated in the furnace. When the niobium used was in the form of a powder, which oxidizes completely at a temperature as low as 500-530°, the $Nb_2O_5$ prepared from it proved very active.

Thus, when isopropyl alcohol had been passed at 360°, at a rate of flow which was the same in the preceding experiments (0.15 ml/min), over 2 ml of $Nb_2O_5$ prepared by glowing powdered niobium at 530° for 1 hr., up to 40 ml/min of unsaturated hydrocarbon gas were evolved as compared with 1.5 ml/min that were evolved under the same conditions over $Nb_2O_5$ prepared by lengthy glowing of a platelet at 750°. In other words, the degree of conversion increased from 3.4% to 91%. Although the original activity of a sample of this type initially dropped by 20-25% after 30-40 min. of operation, the activity remained sufficiently high afterwards (at a level corresponding to 65-70% of conversion). Heating of the oxide that had formed for a prolonged time (2-3 hrs) at 530° resulted in some reduction of the activity. However, the latter still remained much higher than that of a sample obtained by prolonged high-temperature burning (at a temperature of the order of 750°).

TABLE 2

The Effect of Heating on the Catalytic Activity of $Nb_2O_5$

| Length of heating at 700°, hours | Degree of conversion of i-$C_3H_7OH$, % |
|---|---|
| 2 | 38.2 |
| 4 | 25.6 |
| 6 | 10.0 |

$Nb_2O_5$ prepared by the oxidation of metallic Nb at 600-630° for 1 hr. also proved very active. However, in this case the activity decreased more rapidly from experiment to experiment and an increase of the length of heating to 2-3 hours had a strong effect in lowering the activity by a factor of 3-4. The low activity of the first sample of $Nb_2O_5$ with which the kinetics of dehydration were investigated (sample 1) was due to the fact that it was heated for 5 hours at 750°. As an illustration of the effect which the length of heating of $Nb_2O_5$ at 700° has on its activity one may cite the data listed in Table 2.

It follows from what has been said above that the most active $Nb_2O_5$ samples among those tested were obtained by glowing metallic niobium for 1-2 hours at 530°. One should note in connection with this that a higher or lower rate of formation of the oxide must result depending on the state of the metal which is used — i.e., depending on whether the metal is in the form of a powder, shavings, or larger pieces. For this reason individual experiments carried out with $Nb_2O_5$ prepared, for example, by glowing for 1 hr. at 530°, did not give results which could be regarded as strictly reproducible. However, an active catalyst was obtained in all cases and the activity was preserved for a long time without regeneration; for instance, for a period longer than 10 hours.

The kinetics of the dehydration of isopropyl alcohol were investigated by using one of the active $Nb_2O_5$ samples prepared by us (sample 2). This sample was prepared by oxidizing powdered metallic Nb for 1 hr. at 500-530°. The temperature of the experiments was purposely kept low in order to have a low degree of conversion of the alcohol. This was done because of the considerations mentioned above in regard to the calculation of the energy of activation. The experiments were carried out in the range of 305-329° with a flow rate of the alcohol amounting to 0.15 ml/min and a volume of the loosely packed catalyst equal to 2 ml. The results of the experiments are shown in Table 3 and Fig. 2. Table 3 is arranged similarly to Table 1.

TABLE 3

Dehydration of Isopropyl Alcohol on $Nb_2O_5$ (sample 3) (flow rate of the alcohol 0.15 ml/min; volume of the loosely packed catalyst 2 ml; at a 100% conversion, m = 43.9 ml/min; $\epsilon$ = 23400 cal/M)

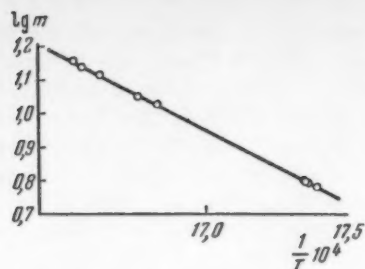| No. of the experiment | Temp. of the expt., °C | m(obs.), ml/min per 1 ml. of catalyst, brought to STP | lg $k_0$ | m calcd. from $\epsilon$ and the mean value of lg $k_0$ | $\frac{\epsilon}{\lg k_0} \cdot 10^{-4}$ |
|---|---|---|---|---|---|
| 8 | 304 | 3,00 | 9,351 | 3,09 | 2,51 |
| 13 | 305 | 3,15 | 9,356 | 3,16 | 2,50 |
| 10 | 320 | 5,45 | 9,370 | 5,37 | 2,50 |
| 2 | 322 | 5,65 | 9,357 | 5,75 | 2,50 |
| 6 | 326 | 6,70 | 9,374 | 6,46 | 2,50 |
| 12 | 328 | 6,80 | 9,351 | 6,92 | 2,51 |
| 15 | 329 | 7,25 | 9,365 | 7,24 | 2,50 |
| | | Mean value | 9,360 | | |

Fig. 2. Dehydration of isopropyl alcohol on $Nb_2O_5$ (sample 2). Relation between lg m and $1/T$.

TABLE 4

Preservation of the Activity of $Nb_2O_5$ (sample 1) according to control tests out at 305°

| No. of expts. | m in ml/min |
|---|---|
| 1 | 6.3 |
| 4 | 6.2 |
| 7 | 6.5 |
| 9 | 6.5 |
| 13 | 6.3 |
| 16 | 6.3 |

The numbers of the experiments correspond to the order in which the experiments were carried out. The dispersion of the numbers is due to the fact that between individual experiments at any temperature the constancy of the activity of the catalyst was checked on the basis of results obtained in experiments carried out at the initial temperatures of 304 and 305°. It can be seen from Table 4 that the activity of the catalyst at 305° remained constant.

It follows from Fig. 2 that the Arrhenius equation also applies to the active $Nb_2O_5$ sample: all values of lg m fitted well on a straight line when they were plotted as a function of $1/T$. The activation energy for the active $Nb_2O_5$ was found to be somewhat lower than for the inactive sample; it was equal to 23.4 kcal/M.

An X-ray phase analysis of the active $Nb_2O_5$ sample in question indicated that this sample also consisted of the low-temperature modification of $Nb_2O_5$ (cf. Table 6). Thus, the same low-temperature modification of $Nb_2O_5$ may exhibit different activities depending on the temperature at which the $Nb_2O_5$ was prepared and the length of time during which it was heated.

Measurements of the adsorption of benzene vapor showed that both samples had practically the same surface (5-7 $m^2/g$), so that the difference in activities cannot be explained by a difference in the magnitude of the surface. Apparently the explanation must be sought in differences of the porosity and of the microroughness on the surface of the oxide. $Nb_2O_5$ prepared by glowing metallic Nb in the range above 850° for 2 hrs, at temperatures reaching 900-950° (sample 3), also showed a low activity, but in this case a different modification of $Nb_2O_5$ was present, as can be seen from the results of the X-ray phase analysis (Table 7).

Results of the X-ray phase analysis of the samples investigated are given below. The x-ray exposures were made by using a Feniks (Phoenix) tube of the type BSV equipped with an iron anode. A potential of 25 kV and a current load of 8 mA were applied. The film was charged asymmetrically into RKD-57 cameras. Only $\alpha$-interferences are listed in the tables.

As has been mentioned above, the results obtained in the X-ray phase analysis of a fresh and a spent sample of $Nb_2O_5$ (sample 1) indicated that both samples had the same crystal structure, because they yielded practically identical X-ray diagrams.

In Table 5, $d_{msd}$ indicates the average result arrived at by carrying out measurements on both exposures. It follows from Table 5 that all lines can be satisfactorly indexed in the rhombic axes $a_1 = 6.14 \pm 0.01$; $a_2 = 3.64 \pm 0.005$; $a_3 = 3.91 \pm 0.005$ kX. These values are close to those of $a_1$, $a_2$, and $a_3$ found by Sellers and co-workers [5] for the low-temperature modification of $Nb_2O_5$, namely $a_1 = 6.19 \pm 0.01$; $a_2 = 3.66 \pm 0.01$; $a_3 = 3.94 \pm 0.01$ kX.

Table 6 lists the results of the X-ray phase analysis of an active sample of $Nb_2O_5$ (sample 2). As can be seen from Table 6, sample 2 also consisted of the Brauer-Sellers low-temperature modification of $Nb_2O_5$ [5]: all the lines for this sample in Table 6 could be satisfactorily indexed in rhombic axes with the dimensions $a_1 = 6.16 \pm 0.005$; $a_2 = 3.651 \pm 0.005$; $a_3 = 3.922 \pm 0.005$ kX, which correspond closely to the dimensions given by Sellers that have been cited above [5]. Finally, Table 6 lists the results of an analysis of an $Nb_2O_5$ sample (sample 3) prepared by glowing metallic Nb at temperatures from 850° to 900-950° for 2 hours.

Zvinchuk [6] established that $830 \pm 5°$ is the transition temperature at which the low-temperature ($\gamma$) modification of $Nb_2O_5$ changes into the medium-temperature ($\beta$) modification, for which he gave the following dimensions of the monoclinic cell: $a = 20.24$; $b = 3.82$; $c = 20.24$ kX; $\beta = 120°$.

The majority of lines in the X-ray analysis diagram for $Nb_2O_5$ (sample 3) corresponded to the data for $\underline{d}$ of Zvinchuk's $\beta$-modification [6]. Most of the remaining lines could be ascribed to the high-temperature modification of $Nb_2O_5$, which was originally reported by Brauer [7]. According to Brauer, this modification is stable at a

## TABLE 5
Results of the X-ray Phase Analysis of $Nb_2O_5$ (sample 1)

| $I$ | $d_{msd}$ | $I/d^2_{msd}$ | $hkl$ | $I/d^2_{calc}$ | $I$ | $d_{msd}$ | $I/d^2_{msd}$ | $hkl$ | $I/d^2_{calc}$ |
|---|---|---|---|---|---|---|---|---|---|
| m.b. | $3,89_3$ | 0,0659 | 001 | 0,0653 | m.w. | 1,626 | 0,3782 | 311 | 0,3791 |
| r.v.w. | $3,65_5$ | 0,0749 | 010 | 0,0753 | m.w. | 1,567 | 0,4073 | 220 | 0,4076 |
| m.b. | $3,13_0$ | 0,1021 | 110 | 0,1018 | v.w. | 1,537 | 0,4233 | 400 | 0,4240 |
| m.w. | $3,05_3$ | 0,1069 | 200 | 0,1060 | r.v.w. | 1,513 | 0,4368 | — | — |
| v.w. | 2,684 | 0,1388 | 011 | 0,1406 | m.w. | 1,457 | 0,4730 | 221 | 0,4729 |
| m.w. | 2,444 | 0,1674 | 111 | 0,1671 | r.v.w.,b | 1,432 | 0,4945 | — | — |
| m.w. | 2,42 | 0,1708 | 201 | 0,1713 | r.v.w.,b | 1,414 | 0,5002 | 410 | 0,4993 |
| r.v.w. | 2,34 | 0,1826 | 210 | 0,1813 | r.v.w.,b | 1,392 | 0,5161 | — | — |
| r.v.w. | 2,110 | 0,2246 | — | — | r.v.w.,b | 1,372 | 0,5312 | — | — |
| m.v. | 1,957 | 0,2611 | 002 | 0,2612 | m.w. | 1,334 | 0,5619 | 022 | 0,5628 |
| m.v. | 1,820 | 0,3019 | 020 | 0,3016 | m.w. | $1,399_5$ | 0,5742 | 312 | 0,5750 |
| m.v. | 1,785 | 0,3139 | 310 | 0,3138 | w.,b | 1,303 | 0,5877 | 003 | 0,5877 |
| v.w.,b | 1,724 | 0,3365 | 012 | 0,3365 | m.w. | 1,224 | 0,6675 | 222 | 0,6688 |
| r.v.w.,b | 1,691 | 0,3497 | — | — | m.w.,b | $1,207_5$ | 0,6859 | 402 | 0,6852 |
| m. | 1,662 | 0,3620 | 012 | 0,3630 | m.w. | 1,192 | 0,7038 | 130 | 0,7042 |
| m. | 1,652 | 0,3664 | 021 | 0,3669 | w.,b | 1,141 | 0,7681 | 131 | 0,7695 |

m = medium; m. b. = medium bright; m. w. = medium weak; m.w.,b. = medium weak, broad; r.v.w = reflection very weak; r.v.w.,b. = reflection very weak, broad; v.w. = very weak; v.w.,b. = very weak, broad; w.,b. = weak, broad.

## TABLE 6
Results of the X-ray Phase Analysis of $Nb_2O_5$ (sample 2)

| $I$ | $d_{msd}$ | $I/d^2_{msd}$ | $hkl$ | $I/d^2_{calc}$ | $I$ | $d_{msd}$ | $I/d^2_{msd}$ | $hkl$ | $I/d^2_{calc}$ |
|---|---|---|---|---|---|---|---|---|---|
| v.b. | 3,92 | 0,0649 | 001 | 0,0650 | r.v.w. | 1,629 | 0,3768 | 311 | 0,3772 |
| v.b. | 3,14 | 0,1012 | 110 | 0,1013 | r.v.w. | 1,571 | 0,4052 | 220 | 0,4054 |
| w. | 3,07 | 0,1059 | 200 | 0,1054 | r.v.w. | 1,540 | 0,4217 | 400 | 0,4218 |
| b. | 2,449 | 0,1667 | 111 | 0,1664 | m.w.,b | 1,460 | 0,4691 | 221 | 0,4704 |
| w. | 2,420 | 0,1708 | 201 | 0,1704 | r.v.w.,b | 1,336 | 0,5603 | 022 | 0,5600 |
| m.b. | 1,962 | 0,2598 | 002 | 0,2600 | v.w.,b | 1,322 | 0,5722 | 312 | 0,5722 |
| m.w. | 1,826 | 0,2999 | 020 | 0,3000 | r.d.,v.w. | 1,307 | 0,5854 | 003 | 0,5850 |
| m.w. | 1,792 | 0,3114 | 310 | 0,3122 | w.,b | 1,227 | 0,6640 | 222 | 0,6654 |
| r.d.,r.w. | 1,733 | 0,3330 | 012 | 0,3350 | m.b. | 1,194 | 0,7014 | 130 | 0,7014 |
| m. | 1,663 | 0,3616 | 112 | 0,3613 | w.,b | 1,142 | 0,7654 | 131 | 0,7664 |
| m. | 1,652 | 0,3664 | 021 | 0,3650 | | | | | |

b. = bright; m. = medium; m.b. = medium bright; m.w. = medium weak; m.w.,b = = medium weak, broad; r.d., v.w. = reflection distinct, very weak; r.v.w. = reflection very weak; r.v.w. = reflection very weak; r.v.w., b = reflection very weak, broad; v.b. = very bright; v.w.,b = very weak, broad; w. = weak; w., b. = weak, broad.

temperature of approximately 1200°. These results are of independent value, because they indicate that during the isomeric process of the oxidation of Nb strong local overheating may arise and bring about at 950° partial formation of a modification which is stable at 1200°.

Tantalum pentoxide. The tantalum pentoxide was prepared by glowing finely cut platelets of metallic tantalum in a muffle furnace for 3-4 hrs. at 700-750°, which in this case led to the conversion of all of the metal into oxide. Investigation of the kinetics of dehydration of isopropyl alcohol on $Ta_2O_5$ was carried out in the same equipment in which the work with $Nb_2O_5$ had been done. Measurements were made in the temperature range of 336-383° at a rate of flow of the alcohol amounting to 0.2 ml/min. The volume of the catalyst (loosely packed) was 2 ml, the volume velocity of the alcohol 6.0 hrs$^{-1}$. Before an experiment every sample was activated with an air current at 410° for 2 hrs. Measurements of the evolved gas were carried out in the same manner as in experiments with $Nb_2O_5$ and the duration of the experiments was the same.

According to the results of the gas analysis, the gas, which evolved at a uniform rate, consisted to the extent of 98.6-98.9% of propylene. The activity of the $Ta_2O_5$ catalyst did not remain constant for a long time. No precise relationships with respect to the changes in the activity of $Ta_2O_5$ during its use as a catalyst could be established. However, the following observations were made: after 3-4 experiments of 30 min. each the activity of the catalyst decreased by approximately 30%, and during the following 3-4 experiments of 30 min. each this reduced

TABLE 7

Results of the X-ray Phase Analysis of $Nb_2O_5$ (sample 3)

| Our data | | Zvinchuk's data (β-modification) | | Brauer's data (H-modification) | |
|---|---|---|---|---|---|
| I | d | I | d | I | d |
| m. | 3,74 | 10 | 3,73₅ | v.b. | 3.62 |
| v.w. | 3,60 | | | | |
| m.w. | 3,56 | 10 | 3,57₆ | | |
| r.v.w. | 3,49 | 2 | 3,50 | b. | 3.47 |
| r.v.w. | 3,37 | | | | |
| w.,v.b. | 3,08 | | | | |
| r.d.,v.b. | 2,93 | 1 | 2,97 | | |
| v.w. | 2,81₅ | | | m. | 2.81 |
| m.w. | 2,77₅ | 8 | 2,771 | | |
| r.v.w. | 2,705 | | | m.w. | 2.69 |
| w.,v.b. | 2,538 | 4 | 2,530 | | |
| v.w. | 2,492 | 2 | 2,504 | | |
| m.w. | 2,311 | 5 | 2,302 | m.w. | 2.305 |
| m.w. | 2,054 | 6 | 2,051 | | |
| m. | 1,909 | 2 | 1,910 | m.b. | 1.903 |
| r.d.,v.b. | 1,818 | | | w. | 1.812 |
| w.,v.b. | 1,786 | 4 | 1,779 | w. | 1.782 |
| m.b. | 1,685 | 7 | 1,687 | w. | 1.685 |
| r.d.,v.b. | 1,663 | | | b. | 1.671 |
| m. | 1,579 | 6 | 1,574 | m. | 1.573 |
| r.d.,v.b. | 1,558 | | | m.b. | 1.561 |
| w. | 1,526 | 4 | 1,525 | | |
| v.w. | 1,515 | | | v.w. | 1.511 |
| r.v.w. | 1,452 | 4 | 1,455 | | |
| r.d.,v.b. | 1,436 | | | | |
| m. | 1,398 | 6 | 1,398 | | |
| m.w. | 1,304 | 4 | 1,303 | | |
| m.w. | 1,277 | 2 | 1,281 | | |
| m.w. | 1,268 | 2 | 1,265 | m.w. | 1.270 |
| r.v.w. | 1,252 | | | | |
| m.w. | 1,215 | 3 | 1,215 | | |
| m.w. | 1,165 | 2 | 1,165 | | |
| m.w. | 1,154 | 2 | 1,151 | | |
| m.w. | 1,132 | 1 | 1,138 | | |
| m. | 1,075 | 3 | 1,076 | | |

b. = bright; m. = medium; m.b. = medium bright; m.w. = medium weak; r.d.,v.b. =
= reflection distinct, very broad; r.v.w. = reflection very weak; v.b. = very bright;
v.w. = very weak; w. = weak; m.,v.b. = weak, very broad.
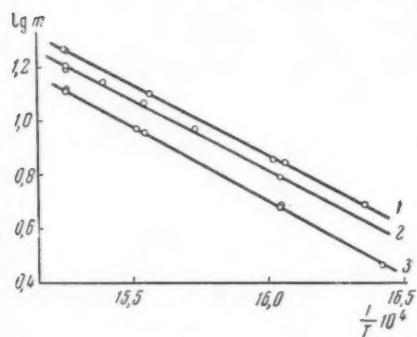


Fig. 3. Dehydrogenation of isopropyl alcohol on $Ta_2O_5$. Relation between lg m and 1/T for samples; 1) with the initial activity; 2) after restoration; 3) with lowered activity.

activity remained constant. Regeneration of the catalyst in an air current at 410° for 2-10 hrs. resulted in an increase of the activity to approximately 85% of its initial level (see straight line 2 in Fig. 3).

Lowering of the activity also occured every time when the catalyst was let to stand overnight after completion of an experiment and cooling of the system with a stream of air. One must mention two points with respect to the regeneration of a sample of this type. If during the experiments no lowering of the catalyst's activity had taken place, letting the catalyst stand overnight resulted in a decrease of the activity by approximately 30% (cf. straight line 3 in Fig. 3). However, if the catalyst was regenerated by air at 400° for 2 hrs, it was restored to exactly the same activity which was obtained by the regeneration mentioned above (line 2 in Fig. 3). On the other hand, if one let stand overnight a catalyst the activity of which had already decreased somewhat, regeneration of a catalyst sample of this type even for a long period of time (up to 10 hrs.) had no effect whatever and even led to a still greater reduction of the activity. Repeated glowing of a sample with a lowered activity in a muffle furnace did not contribute to its regeneration.

## TABLE 8

Dehydration of Isopropyl Alcohol on $Ta_2O_5$ (flow rate of the alcohol 0.2 ml/min; volume of the loosely packed catalyst 2 ml; at a 100% conversion, m = 58.6 ml/min; $\epsilon_I$ = 23800 cal/M; $\epsilon_{II}$ = 25400 cal/M)

| Number of experiment | Temp. of the experiment, °C | m(obs.), ml/min per 1 ml of catalyst, brought to STP | lg $k_0$ | m calculated from $\epsilon$ and the mean value of lg $k_0$ | $\dfrac{\epsilon}{\lg k_0} \cdot 10^{-3}$ |
|---|---|---|---|---|---|
| For fresh samples with a maximum activity |
| 2 | 338 | 2,45 | 8,916 | 2,42 | 2,67 |
| 4 | 349 | 3,50 | 8,916 | 3,46 | 2,67 |
| 6 | 351 | 3,55 | 8,895 | 3,68 | 2,68 |
| 7 | 369 | 6,25 | 8,907 | 6,31 | 2,67 |
| 5 | 382 | 9,25 | 8,916 | 9,14 | 2,67 |
| 3 | 382 | 9,15 | 8,911 | 9,14 | 2,67 |
| 1 | 382 | 9,20 | 8,914 | 9,14 | 2,67 |
| | Mean | Mean value | | | |
| For samples with a lowered activity, II |
| 11 | 336 | 1,45 | 9,237 | 1,48 | 2 73 |
| 20 | 336 | 1,45 | 9,287 | 1,48 | 2 73 |
| 12 | 350 | 2,40 | 9,301 | 2,37 | 2,73 |
| 15 | 370 | 4,50 | 9,300 | 4,46 | 2,73 |
| 18 | 371 | 4,75 | 9,307 | 4,63 | 2,73 |
| 10 | 382 | 6,40 | 9,291 | 6,47 | 2,73 |
| 17 | 382 | 6,50 | 9,298 | 6,47 | 2,73 |
| | | Mean value | 9,296 | | |

## TABLE 9

Dehydration of Isopropyl Alcohol on $Ta_2O_5$ after Regeneration of This Catalyst (flow rate of the alcohol 0.2 ml/min; volume of the loosely packed catalyst 2 ml; at a 100% conversion, m = 58.6 ml/min; $\epsilon$ = 23800 cal/M)

| Number of experiment | Temperature of experiment, °C | m(obs.), ml/min per 1 ml of catalyst, brought to STP | lg $k_0$ | m calculated from $\epsilon$ and the mean value of lg $k_0$ | $\dfrac{\epsilon}{\lg k_0} \cdot 10^{-3}$ |
|---|---|---|---|---|---|
| 2 | 349 | 2,80 | 8,819 | 2,97 | 2,70 |
| 5 | 370 | 5,85 | 8,866 | 5,56 | 2,68 |
| 3 | 377 | 6,95 | 8,854 | 6,81 | 2,69 |
| 1 | 382 | 7,70 | 8,836 | 7,84 | 2,69 |
| 4 | 382 | 7,90 | 8,848 | 7,84 | 2,69 |
| | | Mean value 8,845 | | | |
| 21 | 350 | 3,10 | 8,850 | 3,06 | 2,69 |
| 22 | 362 | 4,65 | 8,868 | 4,41 | 2,68 |
| 20 | 382 | 7,55 | 8,828 | 7,84 | 2,69 |
| 23 | 382 | 7,50 | 8,825 | 7,84 | 2,69 |
| 27 | 382 | 7,50 | 8,825 | 7,84 | 2,69 |
| 28 | 350 | 2,95 | 8,829 | 3,06 | 2,69 |
| | | Mean value 8,838 | | | |

An x-ray phase analysis of fresh and used $Ta_2O_5$ showed that both samples belonged to the same modification described by Sellers [5] and consequently had the same crystal structure. Lowering of the activity of the catalyst, particularly after it had been kept overnight, possibly took place because of a polymerization of reaction products on its surface. A conclusion to the effect that chromium oxide catalysts are inactivated as a result of a polymerization of olefins had already been made by one of the authors of this article in earlier work [8]. Recently Topchiev and co-workers [9] described a polymerization of ethylene on chromium oxide at atmospheric pressure which led to an inactivation of this catalyst.

The fact that glowing of inactivated $Ta_2O_5$ in a muffle furnace did not restore fully the activity of this catalyst, although any film of organic matter that had formed must have been burned off, can be explained in the following manner. Combustion of the film evolves heat, so that local overheating takes place, with the result that there is inactivation in spots and general lowering of the activity. Inactivation of catalysts as a result of local overheating was also observed by us in connection with the formation of the high-temperature modification of $Nb_2O_5$ following oxidation of Nb (see above). The inactivation of $Nb_2O_5$ during catalysis can apparently also be explained by the formation of high-polymer films.

Because of the facts presented above in regard to the activity of $Ta_2O_5$, we had to investigate repeatedly fresh portions of this catalyst in order to obtain the necessary data for the calculation of the activation energy, so as to get adequate information for a sample with a constant initial activity, one with a constant lower activity, and one with a constant catalytic activity after regeneration. The results of the experiments are shown in Tables 8 and 9 and in Fig. 3. It follows from the results listed in the upper part of Table 8 that the maximum degree of conversion of alcohol in the experiments conducted up to the temperature of 351° was low and did not exceed 12.1%; consequently the quantity of evolved gas m (in ml/min) could be regarded as equal to the velocity constant $\underline{k}$ of the reaction. By representing graphically Arrhenius' relationship on the basis of the $\underline{m}$ values determined at all temperatures under investigation from 338 to 382° for the three samples mentioned above, we found that all points (not only those corresponding to the lower temperatures) fitted smoothly on straight lines, so that the Arrhenius equation could be regarded as valid. It followed from this that even at high degrees of conversion $\underline{m}$ was close to $\underline{k}$. Hence, on the basis of the experimental data which were available, activation energies $\epsilon$ could be determined which differed little from the true energies of activation. The activation energy for the dehydration of isopropyl alcohol on $Ta_2O_5$ proved to be 23.8 kcal/M in the cases of the fresh and the regenerated sample. In the case of the sample which had been used without regeneration and which had a constant, but lowered activity, the energy of activation was 25.4 kcal/M. Thus, samples with a lowered activity had a higher energy of activation than fresh samples. Regeneration brought the activation energy of a sample back to its original value.

At a constant $\epsilon$, the values of lg $k_0$ remained sufficiently constant; the dispersion of values was somewhat greater than with $Nb_2O_5$, apparently because of the fact that the catalytic activity of $Ta_2O_5$ was less constant than that of $Nb_2O_5$. The calculated values of $\underline{m}$ (Table 9 column 5) were in good agreement with the observed values (column 3). The logarithmic relation was also found to be valid in the case of $Ta_2O_5$. The ratio of $\epsilon$ / lg $k_0$ remained constant, but had on the average a somewhat lower value than in the case of $Nb_2O_5$: it was equal to 2.70.

As a result of a comparison of the catalytic activities of $Nb_2O_5$ and $Ta_2O_5$ determined at the same temperatures, the conclusion could be made that under the same conditions, and specifically in the same temperature range, $Ta_2O_5$ was evidently more active than $Nb_2O_5$ (cf. data listed in Tables 1 and 8). The higher activity of $Ta_2O_5$ in comparison with that of $Nb_2O_5$ was accompanied by a lower energy of activation. On the other hand, $Nb_2O_5$ preserved its activity for a longer time and could be regenerated with greater facility than $Ta_2O_5$.

At present we are continuing an investigation of the effects which the temperature and length of heating of $Ta_2O_5$ following its formation from the metal have on the catalytic activity, and also of the effect which the factors mentioned exert on the activities of $Nb_2O_5$ and $Ta_2O_5$ with respect to other reactions, specifically that of condensation.

To be able to calculate the energies by which three atoms, in this case C, H, and O, are bound to the catalysts $Nb_2O_5$ and $Ta_2O_5$, one must know the activation energies of three reactions the index of which includes these atoms. Because the pentoxides of niobium and tantalum, which have been investigated, proved to be practically inactive with respect to the dehydrogenation of either alcohols or hydrocarbons, the problem arises of finding other reactions with indices including the same atoms. One of the possibilities is the reaction of aldehyde condensation, because, as has been found by Balandin [10], the pentoxides of niobium and tantalum are capable of catalyzing this reaction. The process then proceeds in a highly selective manner: for instance, in the case of acetaldehyde, the reaction

results almost exclusively in the formation of croton aldehyde. Taking advantage of this circumstance, we have now begun a determination of the kinetics of the condensation of aldehydes with the purpose stated above.

Laboratory Technician Z. M. Skur'skaya took a prominent part in the experimental work conducted in connection with this investigation. We are taking the opportunity of expressing our thanks to A. E. Agranomov for determining the catalyst surfaces by the BET method and to V. M. Akimov for carrying out the X-ray analysis of $Ta_2O_5$.

## SUMMARY

1. The activation energy of the dehydration of isopropyl alcohol on two samples of niobium pentoxide with different activities ($\epsilon$ = 23.4 and 27.0 kcal/M) and on tantalum pentoxide ($\epsilon$ = 23.8 kcal/M) was determined. The action (reaction velocity) constants and the constants of the logarithmic dependence were determined.

2. It was found that the activity of $Nb_2O_5$ depends to a great extent on the temperature of glowing and duration of the glowing to which the oxide has been subjected in connection with its preparation from the metal. The most active sample of $Nb_2O_5$ was obtained by glowing metallic Nb at 530° for 1 hr.

3. On the basis of data obtained in X-ray phase analysis, the catalytically more active form of $Nb_2O_5$ was found to consist of the low-temperature $\gamma$-modification. The high-temperature modification of $Nb_2O_5$ proved to be less active. There was no change of the $Nb_2O_5$ to another modification during the dehydration of the alcohol under the conditions studied.

4. $Ta_2O_5$ prepared under comparable conditions was found to be more active than $Nb_2O_5$.

5. It was established that catalysts consisting of pure $Nb_2O_5$ or $Ta_2O_5$ can be regenerated. The conditions of their regeneration with air were investigated.

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# "REGULARITIES IN THE CATALYTIC DEHYDROGENATION OF PRIMARY AND SECONDARY ALCOHOLS"

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No publications exist in the literature which describe a systematic investigation of the kinetics of dehydrogenation of alcohols on the same oxide catalyst. As far as dehydrogenation of alcohols on a copper-chromium catalyst is concerned, the authors of an article on the subject [1] state that the extent of dehydrogenation, which was determined on the basis of the yields of the corresponding aldehydes and ketones, decreased with the increase in the molecular weight of primary and secondary alcohols subjected to dehydrogenation. The degree of conversion of secondary alcohols was found to drop rapidly with the reduction of the symmetry of the molecule. Thus, the authors established that the degree of conversion of isopropyl alcohol was greater than that of secondary butyl alcohol.
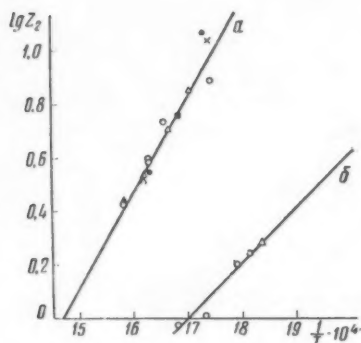


Fig. 1. Dependence of lg $z_2$ on $1/T$:
a) for primary alcohols; b) for secondary alcohols.

In earlier communications [2, 3] we reported experimental data obtained in the investigation of the kinetics of dehydrogenation of primary and secondary alcohols with a straight-chain and branched structure. All investigations were conducted with the use of a single sample of an oxide catalyst. The relative adsorption coefficients of the aldehydes and ketones were determined. It was found that the relative adsorption coefficients ($z_2$) of the carbonyl compounds in the first approximation do not depend on the length of the chain, and decrease considerably with the degree of branching. The relative adsorption coefficients of the ketones were found to be lower than those of the aldehydes. It was established that there is a linear relation between lg $z_2$ and the inverse absolute temperature. The slope of the straight line expressing this relation corresponded to the difference between the heat of adsorption of the aldehyde or ketone and that of the alcohol. The slope of the straight line was greater in the case of primary alcohols than that of secondary alcohols (cf. Fig. 1). The numerical values of the relative adsorption coefficients which had been determined made it possible to calculate the change in free energy $\Delta F$, the heat content $\Delta H$, and the entropy $\Delta S$ of the adsorption displacement from the active centers of the catalyst.

This article discusses kinetic data obtained by us earlier on the dehydrogenation of primary and secondary alcohols with normal and branched structure [2, 3].

The kinetic data were determined in the temperature range of 300-360° for primary alcohols and that of 280-320° for secondary alcohols. The velocity of the reaction was determined on the basis of the number of milliliters of hydrogen which evolved per minute per one milliliter of the catalyst. One must note that there was a close correspondence between the quantity of hydrogen that had evolved and the quantity of aldehyde or ketone that had formed [2, 3]. The velocity constant of the reaction was calculated from the experimental data by employing an equation which had been given earlier [4, 5]. The values for the reaction velocity constants which were found are listed in Tables 1 and 2. One can see from Fig. 2, in which the velocity constants for the alcohols investigated, as reported in articles [2, 3], are plotted along the axis of ordinates and the temperatures along the axis of abscissae, to what extent the molecular structure of the alcohols affects the velocity of their dehydrogenation. As can be seen from Fig. 2, the velocity constants of the dehydrogenation of normal primary alcohols are close to each other. These

## TABLE 1

Velocity Constants and Activation Energies of the Dehydrogenation of Primary Alcohols with Normal and Branched Structure

| Alcohol | $k_C$, ml/min/ml | | | $\epsilon$, kcal/M | lg $k_0$ | $\epsilon$/lg $k_0 \cdot 10^2$ |
|---|---|---|---|---|---|---|
| | 320° | 345° | 360° | | | |
| Ethyl | 1,22 | 2,01 | 2,79 | 15,9 | 5,93 | 2,68 |
| Propyl | | 1,65 | 2,2 | 15,6 | 5,74 | 2,7 |
| Butyl | 0,95 | 1,7 | 2,2 | 16,3 | 6,0 | 2,71 |
| Amyl | 1,54 | 2,52 | 3,49 | 15,4 | 5,86 | 2,62 |
| Hexyl | 1,05 | 1,92 | 2,48 | 15,6 | 5,81 | 2,68 |
| Heptyl | 1,51 | 2,55 | 3,53 | 15,3 | 5,83 | 2,62 |
| Octyl | 1,22 | 2,18 | 2,94 | 15,6 | 5,86 | 2,66 |
| Nonyl | 1,16 | 1,96 | 2,57 | 15,3 | 5,71 | 2,67 |
| 2-Ethylhexyl | 1,96 | 3,3 | 4,57 | 14,3 | 5,58 | 2,56 |
| | 0,85 | 1,38 | 1,93 | 16,1 | 5,84 | 2,75 |

## TABLE 2

Velocity Constants and Activation Energies of the Dehydrogenation of Secondary Alcohols with Normal and Branched Structure

| Alcohol | $k_C$, ml/min/ml | | | $\epsilon$, kcal/M | lg $k_0$ | $\epsilon$/lg $k_0 \cdot 10^2$ |
|---|---|---|---|---|---|---|
| | 285° | 300° | 320° | | | |
| Isopropyl | 1,44 | 1,96 | 2,86 | 12,8 | 5,18 | 2,47 |
| Butyl | 1,98 | 2,72 | 3,8 | 11,3 | 4,75 | 2,37 |
| Octyl | 1,12 | 1,51 | 2,21 | 13,2 | 5,22 | 2,52 |
| Diisopropyl | 2,58 | 3,39 | 4,88 | 11,5 | 4,92 | 2,33 |

constants increase considerably on transition from primary to secondary alcohols. The velocity constant of the dehydrogenation of isopropyl alcohol, which has a symmetrical structure, was found to be lower than that of the dehydrogenation of secondary butyl alcohol, as distinguished from the result obtained in article [1]. The velocity constant was almost twice as large in the case of secondary butyl alcohol as in that of secondary octyl alcohol, which has a higher molecular weight. Comparison of the velocities of dehydrogenation of primary and secondary alcohols with the same number of carbon atoms in the molecule shows that under identical conditions the velocity of dehydrogenation of isopropyl alcohol is three times as great than that of normal propyl alcohol. For an alcohol with four carbon atoms in the molecule the velocity becomes four times as great, whereas it is only 1.8 times as great when the molecular weight is increased and the alcohol contains eight carbon atoms in the molecule. When the dependence of lg $k_C$ on the inverse absolute temperature is plotted, parallel straight lines are obtained (cf. Fig. 3): there are no deviations from the Arrhenius equation.

The activation energy ($\epsilon$) was calculated from the velocity constants. For primary alcohols of normal structure $\epsilon$ was 15.3-16.3 kcal/M and remained rather constant with a change from two to nine of the number of carbon atoms in the alcohol molecule. A constant energy of activation was observed earlier [6, 7] when primary alcohols of normal structure with a number of carbon atoms in the molecule from one to five were dehydrogenated on copper. The activation energy of secondary alcohols with a straight-chain structure was found to be 11.3-13.2 kcal/M in the present work. The pre-exponential factor had a rather constant value: lg $k_0$ changed from 5.71 to 6.0 in the case of primary alcohols and from 4.75 to 5.22 in the case of secondary alcohols.

In communication [8] the effect of the nature of the substituent on the energy of activation was discussed. For the purpose of treatment of this subject, ethyl alcohol was taken as the initial substance. Its energy of activation, determined from data obtained in the dehydrogenation of aqueous 96% alcohol, was found to be $\epsilon$ = 17.7 kcal/M.
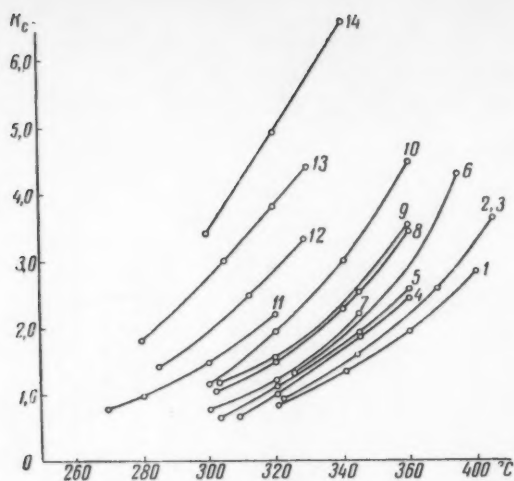
Fig. 2. Effect of the temperature on the dehydrogenation velocity constant: 1) isobutyl; 2) butyl; 3) propyl; 4) hexyl; 5) nonyl; 6) ethyl; 7) octyl; 8) heptyl; 9) amyl; 10) ethylhexyl; 11) sec. octyl; 12) isopropyl; 13) sec. butyl; 14) diisopropyl alcohol.
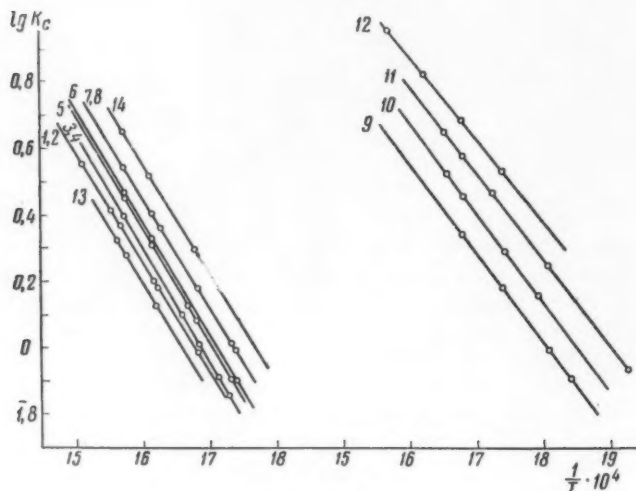


Fig. 3. Relation between lg $k_c$ and $1/T$: 1) n-propyl; 2) n-butyl; 3) nonyl; 4) hexyl; 5) ethyl; 6) n-octyl; 7) amyl; 8) heptyl; 9) sec. octyl; 10) isopropyl; 11) sec. butyl; 12) diisopropyl; 13) isobutyl; 14) 2-ethylhexyl alcohol.

It was established in later work [2] that the energy of activation of absolute ethyl alcohol is 15.9 kcal/M. If one takes absolute alcohol with an activation energy equal to 15.9 kcal/M as the initial substance, the relationships found earlier in regard to the effect which the nature of the substituent has on the energy of activation remain valid, except that some changes in the numerical values must be made: all $\delta\epsilon$ are reduced by a constant value, namely 1.8 kcal/M. Thus, for isopropyl alcohol $\delta\epsilon$ becomes 3.1 instead of 4.9 kcal/M, for n-propyl alcohol 0.3 instead of 2.1 kcal/M, etc.

Fig. 4. Logarithmic relation between $k_0$ and $\epsilon$ : 1) Primary alcohols; 2) secondary alcohols.

It has been found in earlier work [4, 8] that there is a logarithmic relation between $k_0$ and $\epsilon$, as can be seen from Fig. 4, where the energies of activation of the alcohols investigated are plotted along the axis of ordinates and the lg $k_0$ values along the axis of abscissae. All of the points plotted fall on a single straight line. According to Fig. 5, the logarithm of the activity constant lg $k_0$ changes parallel to $\epsilon$.

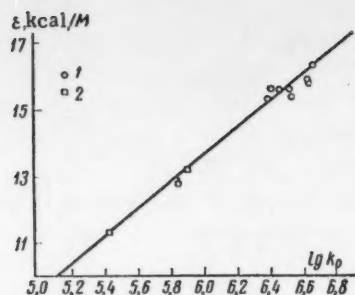As far as the experimental data in regard to adsorption of the active centers of dehydrogenation are concerned, it has been shown in communications [2, 3] that the relative adsorption coefficients of the reaction products are a function of the temperature and that, furthermore, both in the cases of primary alcohols of normal structure and secondary alcohols, these coefficients have under the same conditions numerical values which are close to each other and do not depend on the size of the alcohol molecule. At 345°, the adsorption coefficients of aldehydes were found to change from 3.4-3.5 to 2.6-2.7 at the temperature of 360°. The adsorption coefficients of ketones changed from 1.23 at 300° to 0.8-0.9 at 320°. The change in the heat content comprised 13.5-14.2 kcal/M for primary alcohols and 8.4-11.3 kcal/M for secondary alcohols. As can be seen from Fig. 5, there is a parallelism between $\Delta H$ and $\epsilon$, and also between $\Delta S$, $\Delta H$, and lg $k_0$, which have been plotted in this figure on a different scale.
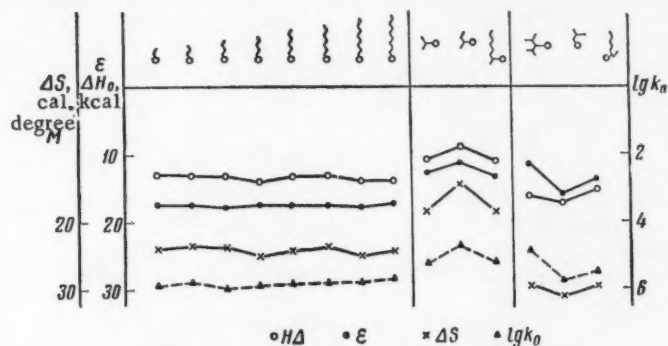


Fig. 5. Parallism between values of $\epsilon$ and lg $k_0$, $\Delta H$ and $\Delta S$, $\Delta H$ and lg $k_0$.

On transition from alcohols with a straight-chain structure to alcohols with a branched structure, the velocity of dehydrogenation of the alcohols increases, as has been brought out in communication [3]. Thus, 2-ethylhexyl alcohol, in which an $\alpha$-hydrogen has been substituted with an ethyl group, is dehydrogenated with a velocity which considerably exceeds that of the dehydrogenation of a straight-chain primary alcohol with the same number of carbon atoms in the molecule. The velocity constant of the dehydrogenation of 2-ethylhexyl alcohol approaches that of the dehydrogenation of secondary octyl alcohol. On the other hand, isobutyl alcohol, in which a hydrogen in the $\alpha$-position has been substituted with a methyl group, is dehydrogenated with a lower velocity than alcohols having a normal (straight-chain) structure. Branching has a still greater effect when two substituents have been introduced. For instance, the velocity constant of the dehydrogenation of diisopropyl alcohol is greater than that of the dehydrogenation of secondary butyl alcohol.

The adsorption characteristics of alcohol with a branched structure differ considerably from those of alcohols with a normal structure. The relative adsorption coefficients of reaction products derived from alcohols with a branched structure are greater, as a consequence of which the free energy, heat content, and entropy of adsorption displacement from the active centers of catalysts are increased. It has been shown in Fig. 5 that the parallelism between the values of $\Delta H$ and $\epsilon$, as well as that between the values of $\Delta S$, $\Delta H$, and lg $k_0$, is also observed in the case of alcohols with a branched structure.

## SUMMARY

1. It has been established that primary alcohols with straight chains from $C_2$ to $C_9$ are dehydrogenated on an oxide catalyst with velocities which are close to each other and that the velocity of the dehydrogenation of secondary alcohols decreases with an increased molecular weight. The velocity of dehydrogenation of alcohols with a branched structure was found to be greater than that of alcohols with a straight-chain structure.

2. It has been found that there is a parallelism between the energy of activation, the pre-exponential factor logarithm, and increments of the heat content and entropy connected with the adsorption displacement of alcohols by the corresponding aldehydes and ketones from the active dehydrogenation centers of the catalyst.

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# "CHEMICAL CORRESPONDENCE IN HETEROGENEOUS CATALYSIS"

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The majority of present-day theories of heterogeneous catalysis, in treating the problem of the selection of catalysts for a definite chemical reaction, do not take into consideration the chemical nature and chemical specificity of the catalizing surfaces. The two most important problems, that of the nature of the active centers and that of the mechanism of catalytic reactions, have been customarily solved under consideration of the geometric and physical properties of surfaces only: the chemical properties of these surfaces were completely disregarded. In treating the energy changes involved in reactions, many authors emphasized the purely quantitative aspects of phenomena and did not pay attention to the qualitative, chemical nature of the chemisorption bonds that are formed between reacting and catalyzing atoms. It seems that the only exception is the theory advanced by Dowden [1, 2-3], which points out that valency d-electrons must be present in the outer electron shell of the atoms (or ions) of the catalyst in order that some reactions take place. This concept received experimental confirmation in work done by Dilke, Maxted, Eley, and Couper [4, 5], Reynolds [6], and Beeck [7], to give a few instances. However, this approach has the shortcoming that the presence of d-electrons is required and that an assumption is made in regard to a continuous change in catalytic activity as the number of vacancies in the d-zone (the number of vacant d-orbitals of atoms) changes. We shall return to this question in the subsequent discussion.

The fact remains that chemisorption of the reacting molecules constitutes a necessary stage of every heterogeneous catalytic reaction: the atoms of the catalyst enter into the composition of an intermediate complex and the chemical nature of the adsorbent must be considered in order that the mechanism of the reaction may be clarified. In our opinion, chemical correspondence between the reacting molecules and the catalyst is an indispensable condition for the occurrence of a catalytic reaction. For any given reaction, this correspondence is expressed in a definite structure of the electron shell of the catalytically active atoms. Before attempting to discuss actual examples of chemical correspondence and explaining such phenomena as the specificity of catalysis, the presence of active centers with different activities, and the effect of the origin of the catalyst on its activity, one must first consider the chemical nature of the free valencies present on the surface of a catalyst.

## The Nature of Free Valencies on the Surface of a Catalyst

Free valencies of different types are present on the surface of a catalyst. They correspond to different normal and excited valency states of the atoms of the adsorbent; the different types of free valencies form active points with different degrees of activity. The nature of the free valency determines the energy of the bond formed between the reacting atoms and the atoms of the catalyst. This energy, in turn, affects the energy of activation of the reaction taking place at the active center in question, i.e., it determines the catalytic activity of this center.

Experimentally determined values of the number of vacant d-orbitals in metal atoms, obtained by measuring magnetic saturation moments — such as 2.22 for Fe and 1.71 for Co-, are mean values which characterize the crystal as a whole. Pauling's theory of the metallic state [8-10] (see also [11]), as distinguished from the zone theory, assumes that the valency electrons are located at the individual atoms. A number of outer electrons are taken up by the formation of metal-metal bonds, while other valency electrons are in the so-called atom orbits and may participate in the formation of adsorption bonds. Every atom of a transition metal has a certain number of free d-electrons (atomic d-orbits) which do not participate in bonds responsible for cohesion. However, a crystal may contain atoms which are in different valency states, i.e., which have a different number of unpaired valency electrons. For instance, iron in its normal state consists of two forms, Fe(A) with two unpaired d-electrons which do not participate in cohesion bonds, and Fe(B) with three free d-electrons (atomic d-orbits):

Fe(A) ↑ ↑ · · · | · | · · o

Fe(B) ↑ ↑ ↑ · · | · | · · o
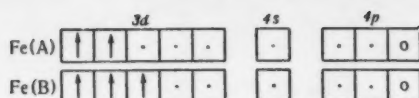
(the electrons which participate in cohesion bonds are indicated by dots; the circles represent metallic orbits which are not occupied by electrons). The proportion of Fe(A) to Fe(B), which is 78 to 22, determines the mean value of 2.22 vacant d-orbits per atom. Furthermore, when the absolute temperature of the surface of iron is higher than zero, there is a certain probability that different excited valency states may be present. Copper in its ground state has no vacant d-electrons, so that its catalytic activity is due solely to the presence of excited valency states; the catalytic activity then depends on the energy of excitation.

Similarly, in an ionic crystal at an absolute temperature higher than zero there may be redistribution of electrons and charges between ions, which will also result in the formation of new active points, the number of which in this case must depend on the ionizatio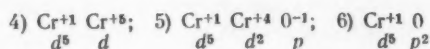n potential. For instance, there is a greater or lesser probability that the following types of active points will be present on the surface of chromium oxide (the number and types of free valencies are shown under the symbol representing the ion*):
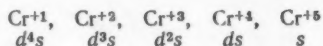
1) most numerous

$$1)\ \underset{d^3}{Cr^{+3}},\ \underset{—}{O^{-2}};\quad 2)\ \underset{d^4}{Cr^{+2}},\ \underset{p}{O^{-1}};\quad 3\ \underset{d^4}{Cr^{+2}}\ \underset{d^2}{Cr^{+4}}$$

2) less probable

$$4)\ \underset{d^5}{Cr^{+1}}\ \underset{d}{Cr^{+5}};\quad 5)\ \underset{d^5}{Cr^{+1}}\ \underset{d^2}{Cr^{+4}}\ \underset{p}{O^{-1}};\quad 6)\ \underset{d^5}{Cr^{+1}}\ \underset{p^2}{O}$$
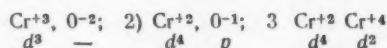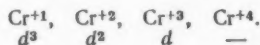
The formation of different configurations with $Cr^0$ is still less probable.

Other types of active points are formed by chromium ions in which one of the valency electrons is in the 4s orbit:

$$\underset{d^4s}{Cr^{+1}},\quad \underset{d^3s}{Cr^{+2}},\quad \underset{d^2s}{Cr^{+3}},\quad \underset{ds}{Cr^{+4}},\quad \underset{s}{Cr^{+5}}$$

States may also exist in which two outer electrons form a closed 4s orbit:

$$\underset{d^3}{Cr^{+1}},\quad \underset{d^2}{Cr^{+2}},\quad \underset{d}{Cr^{+3}},\quad \underset{—}{Cr^{+4}}.$$

By approaching the problem from this standpoint, one can explain the effect of the origin of the catalyst on its catalytic activity. Thus, chromium oxide prepared by heating a bichromate must contain a certain amount of un-reduced hexavalent chromium, while $Cr_2O_3$ prepared from salts of trivalent chromium does not contain any $CrO_3$.

The differences in the mechanisms of hydrogenation and dehydrogenation of hydrocarbons and alcohols on oxides and metals can be explained from this point of view by the entirely different character of the O–H and M–H bonds. In the first of these bonds, the positive charge is displaced towards the hydrogen, and in the second, towards the metal. In connection with this, we may note that on the basis of Balandin's data in regard to energies with which reacting atoms are bound to the atoms of the catalyst, reacting hydrogen atoms are bound preferentially to the oxygen or sulfur of the catalyst (cf. our report [12]). Furthermore, the differences in the types of free valencies of the metal atoms or ions exhibited by the two classes of substances mentioned must play a considerable role. The higher temperature of dehydrogenation on oxides as compared with metals is due to the fact that the metal atoms which catalyze the reaction have free valencies in the ground state, whereas a considerable amount of energy is required for the formation of free valencies of oxygen (see more about this in [12]).

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*The fact that the Cr–O bond in $Cr_2O_3$ is not of a purely ionic type does not change the general conclusions arrived at in regard to the number and type of free valencies, because the three d-electrons of the $Cr^{3+}$ ion which are being considered do not participate in the formation of covalent bonds.

Investigations by Beeck, Boreskov, Kemball, Bond, and Mann make it possible to discern some regularities in the variation of catalytic activity among transition metals within a certain period of the periodic system. In the cases of isotope exchange of deuterium with hydrogen [13, 14], ammonia, and ethane [15], hydrogenation of ethylene [7] and acetylene [16], and oxidation of hydrogen [13, 14] on metal catalysts the highest activity is exhibited by metals which have an almost filled d-shell, i.e., the last elements of the 8th group. If the number of valency d-electrons is great, bonds which are too strong are formed by adsorption, with the result that desorption of the reaction products becomes difficult. For instance, in the case of metals of the IV period the activity increases from iron to nickel and drops sharply at copper, which does not have vacant d-orbits in the normal state. An analogous relationship was observed by Dowden, Mackenzie, and Trapnell [17] in connection with the catalysis by oxides of the isotope exchange between hydrogen and deuterium: the greatest activity was exhibited by oxides the metal ions of which have a low number of unpaired d-electrons ($Co_3O_4$, $NiO$, $Cr_2O_3$). When there were no unpaired d-electrons in the metal ions or the number of such electrons was excessive, the oxide showed a low activity.

Specific Catalytic Activities $\omega$ of Metals of the IV Period at 450° with Respect to the Reaction of Ammonia Synthesis (according to Boreskov and Slin'ko [13, 18])

| Metal | Cr | Fe | Co | Ni | Cu |
|---|---|---|---|---|---|
| $\omega$, cm$^3$ $NH_3$/m$^2 \cdot$hr | $1,6.10^{-4}$ | $9,5$ | $3,2.10^{-1}$ | $5,1.10^{-3}$ | $(2.10^{-4})$ |

In the cases of the synthesis of ammonia [13, 14, 18] and isotope exchange in molecular nitrogen [14], reactions in which the chemisorption of nitrogen constitutes the limiting stage [13, 14, 19], the maximum of catalytic activity in the sequence Cr—Fe—Co—Ni—Cu is displaced towards iron (cf. table). No attempts to explain this phenomenon have been made. However, the variation of the catalytic activity of metals of the IV period with respect to all reactions under consideration can be explained readily on the basis of Pauling's theory of the metallic state and of the concept of chemical correspondence between the reacting molecules and the catalyst.

Reactions slowed down by the chemisorption of nitrogen. As has already been pointed out above, chemisorption of nitrogen forms the limiting stage of the reactions of ammonia synthesis and isotope exchange in molecular nitrogen [13, 14, 19]. In order that the trivalent N atoms be bound, presence of three valency electrons in the atoms of the adsorbent is required. We actually find that the maximum catalytic activity with respect to these reactions is exhibited by iron, one of the valency states of which has three vacant unpaired d-electrons. In the second place with regard to activity stands cobalt, the crystals of which consist partly of Co(A) atoms which also have three unpaired d-electrons*.

The third place is occupied by nickel, which consists of two forms: Ni(A), in which the four d-electrons not taken up by the formation of cohesion bonds only two are unpaired, so that one of the metal-metal bonds must be broken in order that chemsorption of nitrogen may take place, i.e., an additional expenditure of energy is required; and Ni(B), in which all d-electrons not taken up by the formation of cohesion bonds are paired:



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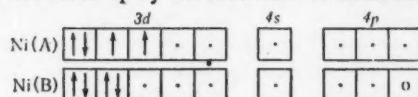
*According to Pauling, cobalt consists of two forms, Co(A) (three vacant atomic d-orbits) and Co(B) (three vacant atomic d-orbits; of the three d-electrons which do not participate in the formation of cohesion bonds two are paired):
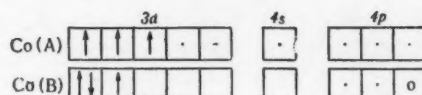


The ratio between these two forms, 35: 65, corresponds to an average number of 1.71 vacant d-orbits per atom.

Copper does not have any unpaired d-electrons, so that its activity is still lower. The chromium modification used by Boreskov (volume-centered A2 cubic lattice) consists essentially of atoms which do not have vacant d-electrons; the small number of atoms with two vacant atomic d-orbitals is responsible for the magnetic moment of 0.22 Bohr magnetrons [8, 9] (this is the value given by Boreskov [13]). In later work Pauling [10] assumed that the chromium modification with the 2A structure consists entirely of atoms all valency electrons of which are taken up by cohesion bonds, i.e., that the magnetic moment is equal to zero. As far as its activity is concerned, chromium is close to copper (cf. table)*.

It is of interest that the catalytic activity decreases together with the average number of vacant atomic d-orbits: Fe 2.22; Co 1.71; Ni 0.6; Cr 0.2 or 0.0 and Cu 0.0.

The variation of catalytic activity with respect to the reactions of ammonia synthesis and of isotope exchange in molecular nitrogen is in accordance with Trapnell's statement [20] to the effect that at low temperatures out of all metals in the sequence Fe—Ni—Cu—Zn only iron is capable of chemically adsorbing nitrogen (no data are given in regard to cobalt)**.

Thus, chemical correspondence between the catalyst and reacting molecules in the case of reactions which are slowed down by the chemisorption of nitrogen is expressed in the requirement that the atoms of the catalyst must have three vacant d-electrons (atomic d-orbits).

Reactions involving chemisorption of hydrogen or deuterium. Shchekin was the first to call attention to the fact that the presence of at least two valency electrons in the atoms of the catalyst is necessary in order that dehydrogenation may take place [21]. It seems to us that this conclusion is completely justified from the standpoint of the multiplet theory of catalysis. Indeed, it is required by this theory that in hydrogenation catalysis two reacting atoms be bound to each atom on an active center of the catalyst with the formation of single bonds. In order that two atoms become attached to an atom of the adsorbent, this atom must have two valency electrons. This also applies to all isotope exchange reactions mentioned above. In the oxidation of hydrogen one atom of the active center binds an O atom, which requires two electrons, while another atom binds two H atoms, which also requires two electrons. Consideration of the nature of the metals which catalyze these reactions indicates that the valency electrons of the adsorbent must be d-electrons. However, absence in the ground state of a pair of valency electrons does not mean that catalysis is impossible. At absolute temperatures higher than zero excitation of valency may take place, so that in a number of cases the necessary quantity of active points with the required number of valency electrons is supplied.

Hydrogenation of aromatic rings takes place on all elements of the 8th group, which have the required quantity of valency electrons in the ground state. It was assumed until recently that iron is not suited for the hydrogenation of benzene; however, in 1950 Beeck and Richie [22] carried out this reaction on an iron catalyst. Of interest is Beeck and Richie's finding to the effect that the dehydrogenation of cyclohexane on tungsten is inhibited because of the the fact that the reaction product (benzene) is strongly adsorbed on the catalyst: tungsten has a great number of valency d-electrons***.

Copper, which does not have any vacant d-electrons in the ground state, cannot catalyze the hydrogenation of aromatic bonds****. However, hydrogenation of the weaker acetylenic bond can be carried out even on copper

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*Chromium crystallizes in three modifications (lattices A2, A3, and A12); in the hexagonal lattice (A3) the chromium atoms have three vacant d-electrons, so that this chromium modification must exhibit a higher activity in reactions involving chemsorption of nitrogen. On the example of chromium one can see the close correlation between the electronic structure and the geometric structure of the catalyst.
**When our article was already in print, communication [30] appeared which reported that the chemsorption of nitrogen takes place at minus 195° on the reduced oxides of iron and cobalt.
***The results obtained by Beeck and Richie are not in accordance with the multiplet theory, which requires that catalysts of the hydrogenation of six-membered cyclic molecules have a face-centered cubic or hexagonal lattice with definite dimensions; from the standpoint of the multiplet theory, iron and tungsten should not catalyze the hydrogenation of benzene. However, it seems to us that the sextet model of the hydrogenation and dehydrogenation of six-membered rings on metal catalyst, which has been postulated by the multiplet theory, cannot be regarded as sufficiently substantiated or proven at this stage (see more about this in ref. [23]).
****This reaction can only be conducted on copper which contains traces of nickel acting as a promoter.

[16], because there is a certain probability that excited atoms which have the necessary quantity of valency electrons will be present on the surface of this metal (copper has a low energy of excitation [20]).

The fact that the maximum of catalytic activity in reactions involving chemisorption of hydrogen or deuterium is exhibited by the last elements of the 8th group can be explained as follows on the basis of Pauling's theory of the metallic state: the ground valency states of the first elements of the 8th group have more than two vacant d-electrons, so that the reacting substances, on being adsorbed, become attached by a strong bond to the surface (for instance, in the case of iron Fe(B) atoms exert a delaying effect*.) Only the crystals of the last elements of the 8th group consist of atoms which do not have more than two valency electrons in the ground state**.

In the dehydrogenation of isopropyl alcohol [28] the maximum catalytic activity in the sequence Fe—Co—Ni—Cu is again exhibited by nickel, but copper is in the second place in this case. This can also be explained by the formation of excessively strong adsorption bonds, with the result that the reaction of iron and cobalt is slowed down. M—O bonds are stronger than M—C bonds, and this presumably brings about a change in the order of catalytic activities when alcohols rather than hydrocarbons are reacted***.

## SUMMARY

1. One must assume that on the surface of metals and ionic crystals there are free valencies of different types, which correspond to normal and excited valency states of the atoms of the adsorbent; different types of free valency represent active points with different activities.

2. The dependence of the catalytic activity on the method by which the catalyst has been prepared can be explained by the circumstance that in addition to the influence of other factors the origin of the catalyst has an effect on the interrelation of different types of free valencies on the catalyzing surface.

3. On the basis of the concept in regard to chemical correspondence between the reacting molecules and the catalyst and Pauling's theory of the metallic state, an explanation has been given to differences in the catalytic activity among metals of the IV period with respect to reactions which are slowed down by the chemisorption of nitrogen and reactions which involve chemisorption of hydrogen or deuterium.

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*If free valencies of Fe(B) are taken up by adsorbed substances, new Fe(B) atoms will form on the surface as a result of the conversion Fe(A) → Fe(B), in view of the fact that the ratio Fe(A):Fe(B) = 78: 22 must be preserved for iron atoms which are not bound to atoms adsorbed on the surface; thus, the number of Fe(A) atoms, from which rapid desorption takes place, decreased in the course of the reaction, so that the effect of these atoms on the catalytic activity can be disregarded when Fe(B) atoms are present.

**If during the oxidation of hydrogen there is chemisorption of hydrogen only or oxygen only, the most active catalyst must again be nickel and the least active copper.

***Beeck [7] and Boudart [29], who applied Pauling's theory of the metallic state to heterogeneous catalysis, considered the relation between the logarithm of the velocity constant of the catalytic reaction and the relative weight of d-states participating in cohesion bonds. However, this approach cannot explain the variation of the catalytic activity in the sequence Cr—Fe—Co—Ni—Cu, because the relative weight of d-states is approximately the same for all of these metals. As has been pointed out by Baker and Jenkins [11], the quantity of d-electrons that are not taken up by cohesion bonds does not, generally speaking, depend on the share of d-electrons in cohesion bonds.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

# SYNTHESIS OF DIALKOXY(OR ARYLOXY)TITANIUM OXIDES
# BY THE TRANSESTERIFICATION OF DIPROPOXYTITANIUM OXIDE

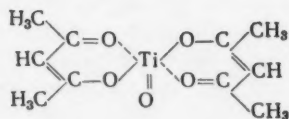A. N. Nesmeyanov, O. V. Nogina, and V. A. Dubovitskii

Up to now only a few dialkoxytitanium oxides $(RO)_2TiO$, a class of compounds which we described for the first time, have been prepared. Dipropoxy- and dibutoxy-titanium oxides were prepared [1] by the oxidation of the corresponding trialkoxytitaniums with oxygen. Somewhat later dipropoxy-, dibutoxy-, diisobutoxy-, di-s-butoxy-, and bis-t-pentyloxy-titanium oxides were synthesized [2] by the hydrolysis of tetraalkoxytitaniums. It should be pointed out that on the basis of molecular-weight determinations Bradley, Gaze, and Wardlaw found that all the dialkoxytitanium oxides obtained by hydrolysis had a polymeric structure. These authors [2] determined the molecular weights of the dialkoxytitanium oxides by cryoscopic and ebullioscopic methods and obtained values indicating a degree of association of 2-4. Our investigations showed [3-5] that in sufficiently dilute solutions dialkoxytitanium oxides are monomeric substances.

We established the identity of the dipropoxytitanium oxide obtained by the oxidation of tripropoxytitanium with the product of the hydrolysis of tetrapropoxytitanium from the infrared absorption spectra of these compounds. The frequencies found in the infrared absorption spectrum of dipropoxytitanium oxide obtained by the oxidation of tripropoxytitanium were 810, 890, 980, 1020, 1080, 1130, 1250, 1380, 1470 $cm^{-1}$, and those found for the dipropoxytitanium oxide obtained by the hydrolysis of tetrapropoxytitanium were 810, 890, 980, 1020, 1080, 1130, 1250, 1370-1384, 1470 $cm^{-1}$.

The method of preparing dialkoxytitanium oxides by the oxidation of trialkoxytitaniums presents considerable experimental difficulties, and the hydrolysis of tetraalkoxytitaniums does not always [2] result in the formation of dialkoxytitanium oxides because the nature of the alkyl group has a substantial effect on the course of the hydrolysis of alkoxytitaniums. We have shown that it is possible to prepare compounds of this class by the esterification of the readily accessible dipropoxytitanium oxide. By this method we prepared diethoxytitanium oxide [6] and the previously undescribed bisisopentyloxy-, bishexyloxy-, bistrimethylsiloxy-, and diphenoxy-titanium oxides. Diphenoxytitanium oxide was isolated also as its molecular compound with phenol.

The infrared absorption spectra of these substances (Figures 1-5) were obtained with a two-beam infrared spectrometer. The substances were taken as solutions in carbon disulfide and carbon tetrachloride, and also as pastes in petrolatum, but in the range 600-1400 $cm^{-1}$ no characteristic frequencies that could be ascribed to the $Ti=O$ bond were detected.

By the reaction of dipropoxytitanium oxide with acetylacetone we synthesized also titanium oxide bisacetylacetonate. This compound was prepared earlier [7] by the hydrolysis of dialkoxytitanium bisacetylacetonates, but the authors considered it to have a cyclic dimeric structure. We established (by comparison of infrared spectra) the identity of the titanium oxide bisacetylacetonate synthesized by the action of acetylacetone on dipropoxytitanium oxide with the substance obtained by hydrolysis. By the determination of the molecular weight of titanium oxide bisacetylacetonate by means of the cryoscopic method in benzene (by the use of methods that we have developed [4, 8]) we showed that, contrary to the conclusions of Jamamoto and Kambara, in dilute solutions this compound is monomeric and evidently has the structure:
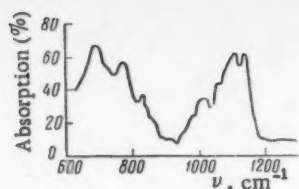
$$\begin{array}{c}H_3C\\HC\\H_3C\end{array}\begin{array}{c}C=O\\\\C-O\end{array}Ti\begin{array}{c}O-C\\\\O=C\end{array}\begin{array}{c}CH_3\\CH\\CH_3\end{array}$$
$$\begin{array}{c}\parallel\\O\end{array}$$

Fig. 1. Infrared absorption spectrum of bisisopentyloxytitanium oxide.



Fig. 2. Infrared absorption spectrum of bishexyl-, oxytitanium oxide $(n-C_6H_{13}O)_2TiO$.
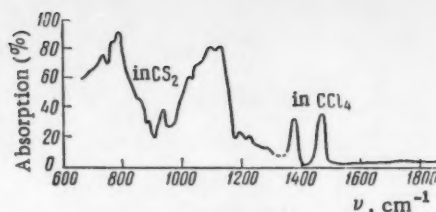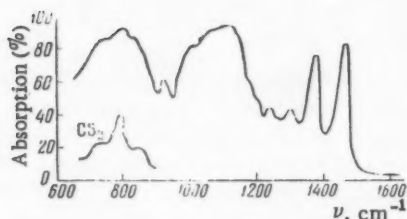


Fig. 3. Infrared absorption spectrum of bis-nonyloxytitanium oxide $(n-C_9H_{19}O)_2TiO$.


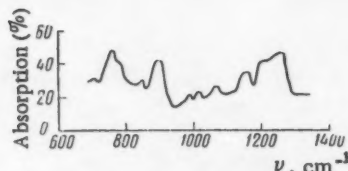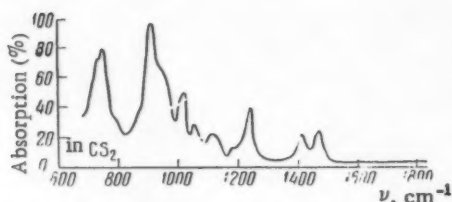
Fig. 4. Infrared absorption spectrum of diphenoxytitanium oxide $(C_6H_5O)_2TiO$.



Fig. 5. Infrared absorption spectrum of bis-triethylsiloxytitanium oxide $[(C_2H_5)_3SiO]_2TiO$.

In an attempt to carry out addition at the double $Ti=O$ bond in titanium oxide bisacetylacetonate (as occurs in the reaction [3] of tetraalkoxysilanes with dialkoxytitanium oxides) the substance isolated was not the addition product, but the dialkoxytitanium bisacetylacetonate, so that the reaction went according to the scheme:

$$(C_5H_7O_2)_2TiO + Si(OR)_4 \rightarrow (C_5H_7O_2)_2Ti(OR)_2 + OSi(OR)_2,$$
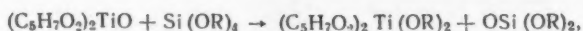
in which $R = C_2H_5$ or $n-C_3H_7$.

## EXPERIMENTAL

All the experiments described below were carried with completely dry substances under conditions excluding access at atmospheric moisture.

Preparation of Diethoxytitanium Oxide by the Action of Ethanol on Dipropoxytitanium Oxide. A solution of 8.4 g (0.046 mole) of dipropoxytitanium oxide in 24 g (0.662 mole) of ethanol was heated for one hour in a bath at 75-80°; a mixture of ethyl and propyl alcohols was then slowly distilled off. A further 24 g of ethanol was added to the reaction mixture, and a mixture of the alcohols was slowly distilled off at a residual pressure of 25-30 mm. The last operation was repeated six times further. To remove traces of alcohols, the residue in the flask was heated in a bath at 100° for 45 minutes at 1 mm. The yield was quantitative. Found: mol. wt. (by the cryoscopic method in benzene) 160; 161; C 31.30; 31.69; H 6.41; 6.36; Ti 31.79; 32.16%. $(C_2H_5O)_2TiO$. Calculated: mol. wt. 154.0; C 31.19; H 6.54; Ti 31.10%. Titanium was determined in a separate sample. Found: Ti 30.72; 31.20%. Calculated: Ti 31.10%.

Preparation of Bisisopentyloxytitanium Oxide. A solution of 17.0 g (0.093 mole) of dipropoxytitanium oxide in 50 g (0.570 mole) of isopentyl alcohol was heated for one hour in a bath at 100°; a mixture of propyl and isopentyl alcohols was then slowly distilled off at a residual pressure of 20-25 mm. A further 34 g of isopentyl alcohol was added, and a mixture of the alcohols was slowly distilled off at 20-25 mm. The last operation was repeated four times further. After distillation of the alcohols the residue in the flask was heated to remove traces of isopentyl alcohol in a bath at 135° for one hour at 1-2 mm. The yield was quantitative. Found: mol. wt. (by the cryoscopic

method in benzene) 248; 246; C 49.67; 49.53; H 9.27; 9.35%. (i-$C_5H_{11}O)_2$TiO. Calculated: mol. wt. 238.2; C 50.43; H 9.31%. Titanium was determined in a separate sample. Found: Ti 20.83; 20.97%. Calculated: Ti 20.11%.

Bisisopentyloxytitanium oxide was obtained as a light-yellow viscous liquid, readily hydrolyzed by atmospheric moisture and decomposed by vacuum distillation. It was readily soluble in all the usual organic solvents.

Preparation of Bishexyloxytitanium Oxide. A solution of 4.0 g (0.022 mole) of dipropoxytitanium oxide in 50 g (0.490 mole) of hexyl alcohol was heated for one hour in a bath at 110°; a mixture of propyl and hexyl alcohols was then slowly distilled off at a residual pressure of 12 mm. A further 50 g of hexyl alcohol was added, and a mixture of the alcohols was slowly distilled off at 12-15 mm. The last operation was repeated twice further. After distillation of the alcohols the residue in the flask was heated to remove traces of hexyl alcohol in a bath at 130-140° for one hour at 1-2 mm. The yield was quantitative. Found: mol. wt. (by the cryoscopic method in benzene) 271; 265; C 53.89; 53.74; H 10.08; 10.12; Ti 17.96; 17.66%. (n-$C_6H_{13}O)_2$TiO. Calculated: mol. wt. 266.2; C 54.13; H 9.84; Ti 17.99%.

Bishexyloxytitanium oxide was obtained as a very viscous liquid, readily hydrolyzed by atmospheric moisture and decomposed by vacuum distillation. It was readily soluble in all the usual organic solvents.

Preparation of Diphenoxytitanium Oxide. Freshly distilled phenol (15.0 g; 0.160 mole) was added to a solution of 7.0 g (0.0385 mole) of dipropoxytitanium oxide in 30 ml of octane. The reaction mixture was heated for one hour in a bath at 110-120°, and a mixture of octane and propyl alcohol was then distilled off at a residual pressure of 20 mm. The excess of phenol was removed by heating the reaction mixture in a bath at 150° for three hours at 1-2 mm. The yield was quantitative; m.p. 197-199°. Found: mol. wt. (by the cryoscopic method in benzene) 241; 245; C 57.67; 57.50; H 4.39; 4.16; Ti 18.90; 18.86%. ($C_6H_5O)_2$TiO. Calculated: mol. wt. 250.1; C 57.63; H 4.03; Ti 19.15%.

Preparation of the Molecular Compound of Diphenoxytitanium Oxide and Phenol. A solution of 0.18 g (0.0019 mole) of phenol in 7 ml of benzene was added to 0.48 g (0.0019 mole) of diphenoxytitanium oxide. The mixture was heated for one hour in a bath at 70°, and benzene was then distilled off. The residue (0.64 g) was crystallized from carbon tetrachloride. This gave light-yellow crystals melting over the range 120-140°. Found: mol. wt. (by the cryoscopic method in benzene) 324; 346; C 62.85; 63.07; H 4.64; 4.64%. ($C_6H_5O)_2$TiO·$C_6H_5$OH. Calculated: mol. wt. 344.2; C 62.81; H 4.68%.

Preparation of Bistriethylsiloxytitanium Oxide. A solution of 12.55 g (0.096 mole) of triethylsilanol in 20 ml of benzene was added dropwise over a period of one hour to a boiling solution of 8.66 g (0.048 mole) of dipropoxytitanium oxide in 50 ml of benzene. A mixture of benzene and propyl alcohol was distilled off at a residual pressure of 30 mm. The residue in the flask was heated to remove traces of benzene and propyl alcohol in a bath at 40-50° for one hour at 2-3 mm. The yield was quantitative. Found: mol. wt. (by the cryoscopic method in benzene) 310; 316; C 45.01, 45.17; H 9.17; 9.34%. [($C_2H_5)_3$SiO]$_2$TiO. Calculated: mol. wt. 326.3; C 44.17; H 9.27%. The product was a light-yellow viscous mass which decomposed when vacuum-distilled.

Preparation of Titanium Oxide Bisacetylacetonate. Freshly distilled acetylacetone (8.6 g; 0.086 mole) was added to a solution of 7.82 g (0.043 mole) of dipropoxytitanium oxide; the mixture became warm. After 30 minutes benzene was distilled off at a residual pressure of 25-30 mm. The residue in the flask was heated to remove traces of solvent in a bath at 50° for three hours at 1.5 mm. The product was crystallized from 8 ml of chloroform and dried on a glass filter with a stream of dry air for two hours. We obtained 5.10 g (45%) of a light-yellow amorphous powder; m.p. 235-236°. The literature [7] gives m.p. 235°. Found: mol. wt. (by the cryoscopic method in benzene) 269; 265; C 45.49; 45.53; H 5.67; 5.53; Ti 18.57; 18.19%. ($C_5H_7O_2)_2$TiO. Calculated: mol. wt. 262.1; C 45.82; H 5.38; Ti 18.28%.

Reaction of Titanium Oxide Bisacetylacetonate with Tetrapropoxysilane. Tetrapropoxysilane (1.43 g; 0.0055 mole) was added to a solution of 1.42 g (0.0055 mole) of titanium oxide bisacetylacetonate in 10 ml of benzene. The mixture was heated for two hours in a bath at 90-100°. Benzene was distilled off at a residual pressure of 25-30 mm. Residual solvent was removed by heating in a bath at 50° for one hour at 1 mm. We obtained a dark-red viscous liquid; its distillation at $10^{-5}$ mm gave a clear light-yellow liquid. Yield 95%. Found: C 52.57; 52.82; H 8.11; 8.13; Ti 13.15; 13.22%. ($C_5H_7O_2)_2$Ti·($OC_3H_7$-n)$_2$. Calculated: C 52.75; H 7.75; Ti 13.15%.

Reaction of Titanium Oxide Bisacetylacetonate with Tetraethoxysilane. Tetraethoxysilane (1.81 g; 0.0087 mole) was added to a solution of 4.55 g (0.0174 mole) of titanium oxide bisacetylacetonate in 15 ml of benzene. The

mixture was heated in a bath at 80° for four hours, and benzene was distilled off at a residual pressure of 25-30 mm. For the complete removal of residual benzene the flask was heated in a bath at 80-90° for two hours at 1-2 mm. We obtained a very thick dark-brown liquid, the distillation of which at $10^{-5}$ mm gave a light-yellow liquid. Found: C 49.66; 49.92; H 7.28; 7.33%. $(C_5H_7O_2)_2Ti(OC_2H_5)_2$. Calculated: C 50.01; H 7.20%.

Titanium was determined in a separate sample by a polarographic method. Found: Ti 13.94; 14.31%. Calculated: Ti 14.30%.

The infrared spectra of samples of dipropoxytitanium oxide prepared by hydrolysis and by oxidation were determined at our request by L. A. Kazitsyna and G. A. Rudenko (Moscow State University), and we express our thanks to them. The infrared spectra of $(i-C_5H_{11}O)_2TiO$; $(n-C_6H_{13}O)_2TiO$; $(n-C_9H_{19}O)_2TiO$; $(C_6H_5O)_2TiO$ and $[(C_2H_5)_3SiO]_2$ TiO were determined in Academician Obreimov's laboratory at the Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR, and for this the authors express their thanks.

## SUMMARY

1. It was shown that dialkoxy(or aryloxy)titanium oxides and bistriethylsiloxytitanium oxide can be prepared by the transesterification of the readily accessible dipropoxytitanium oxide. By this method we synthesized $(C_2H_5O)_2$ TiO, and $(i-C_5H_{11}O)_2TiO$, $(n-C_6H_{13}O)_2TiO$, $(C_6H_5O)_2TiO$, $[(C_2H_5)_3SiO]TiO$.

2. In dilute benzene solution titanium oxide bisacetylacetonate is a monomeric substance.

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# SYNTHESIS OF ORGANOSILICON COMPOUNDS
# CONTAINING PHENYLENESILOXANE MOLECULAR CHAINS

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In previous communications [1-3] we described some organosilicon compounds containing silicon atoms in the para positions in benzene. In the further development of these investigations we examined the hydrolysis of 1-(chloromethylphenylsilyl)-4-(dichlorophenylsilyl)benzene and of p-bis(dichlorophenylsilyl)benzene in an aqueous-ethereal medium. The experiments showed that, unlike trifunctional compounds such as alkyl(or aryl)halosilanes and alkyl-(or aryl)alkoxysilanes, the above compounds, despite their high functionality, do not form high polymers on hydrolysis.

On hydrolysis of 1-(chloromethylphenylsilyl)-4-(dichlorophenylsilyl)benzene in an acid medium, reaction proceeds with formation in 99.1% yield of a crystalline compound in accordance with the scheme:
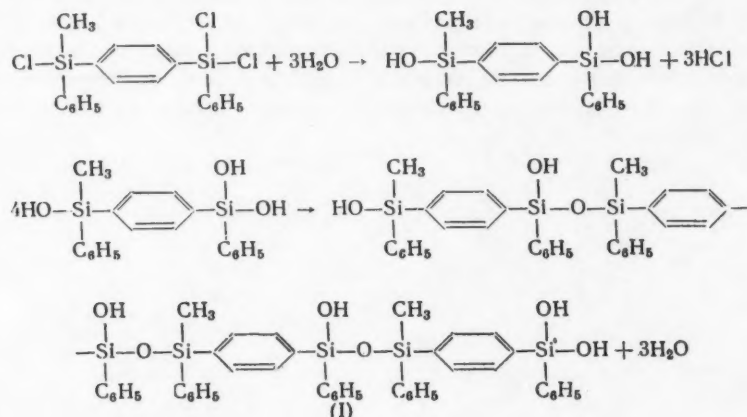


Investigation of this compound showed that it contained 7.5% of hydroxy groups; its molecular weight was 1329. The elementary composition corresponded to the compound (I).

Investigation of the infrared spectrum showed the presence of vibration frequencies corresponding to the bonds

$CH_3-Si$ (800 and 1260 cm$^{-1}$); $C_6H_5-Si$ (483, 743, 1124 and 1421 cm$^{-1}$); $-\langle = \rangle-$ (545 and 1140 cm$^{-1}$);

$HO-Si$ (850-900, ~3400 and 3680 cm$^{-1}$). Moreover, vibration frequencies of $Si-O-Si$ bonds lying in the 1075 cm$^{-1}$ region correspond to a linear compound. This is confirmed also by analytical data on hydroxyl content.

The resulting compound was readily soluble in acetone, benzene, chlorobenzene, toluene, carbon tetrachloride, ether, dioxane, s-tetrachloroethane, chloroform, cyclohexanone, aniline, and cresol. Its melting point was 84-85°. When heated, it readily lost water and was converted into a more complex compound.

On hydrolysis in an acid medium, p-bis(dichlorophenylsilyl)benzene gives a cyclic compound of low molecular weight in 83.5% yield; this is cyclic phenylenebis(hydroxyphenylsilyl)dioxide, formed in accordance with the scheme:

$$\underset{\underset{\text{Cl}}{\overset{\text{C}_6\text{H}_5}{|}}}{\text{Cl}-\text{Si}} \diag<\!\!\diagdown\!\!> \underset{\underset{\text{Cl}}{\overset{\text{C}_6\text{H}_5}{|}}}{\text{Si}-\text{Cl}} + 4\text{H}_2\text{O} \rightarrow \underset{\underset{\text{OH}}{\overset{\text{C}_6\text{H}_5}{|}}}{\text{HO}-\text{Si}} \diag<\!\!\diagdown\!\!> \underset{\underset{\text{OH}}{\overset{\text{C}_6\text{H}_5}{|}}}{\text{Si}-\text{OH}} + 4\text{HCl}$$

(scheme for compound II)

(II)
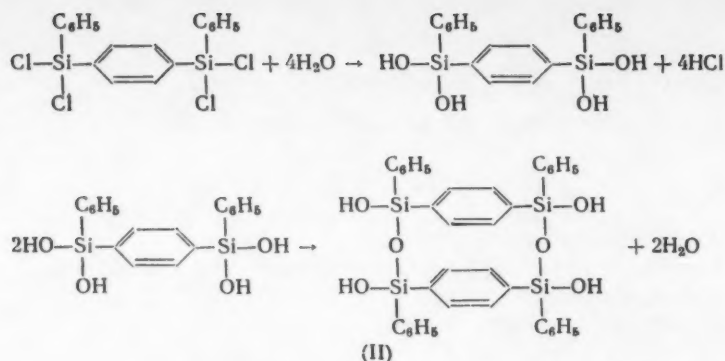
Investigation of the infrared spectrum of this compound showed the presence of vibration frequencies corresponding to the bonds $\text{C}_6\text{H}_5-\text{Si}$ (483, 473, 1124 and 1421 cm$^{-1}$); $-\diagup\!\!\!\diagdown\!-$ (545 and 1140 cm$^{-1}$); HO$-$Si (850-900, ~3400 and 3680 cm$^{-1}$). The vibration frequencies of Si$-$O$-$Si bonds lay in the region 1015-1080 cm$^{-1}$. The elementary composition and molecular weight corresponded to the compound (II).

Cyclic phenylenebis(hydroxyphenylsilyl) dioxide was soluble in the cold in dioxane, acetone, s-tetrachloroethane, ether, aniline, cyclohexanone, chloroform, methanol, and ethanol; it was soluble hot in benzene, toluene, chlorobenzene, and cresol; it was insoluble in carbon tetrachloride, petroleum ether, 1,2-dibromoethane, cyclohexane, octamethylcyclotetrasiloxane, and water. It melted at 93-104°, i.e., when the compound was heated, polycondensation set in. In boiling benzene condensation resulted in the formation of a polymer of molecular weight 3770. We observed that, on being left for a long time as a 50% solution in ether-toluene mixture, cyclic phenylenebis(hydroxyphenylsilyl) dioxide condenses and becomes insoluble. According to the results of elementary analysis and of infrared-spectrum determinations the condensation of this compound leads to the formation of a bisheterocycle in accordance with the equation:

(scheme for compound III)

(III)
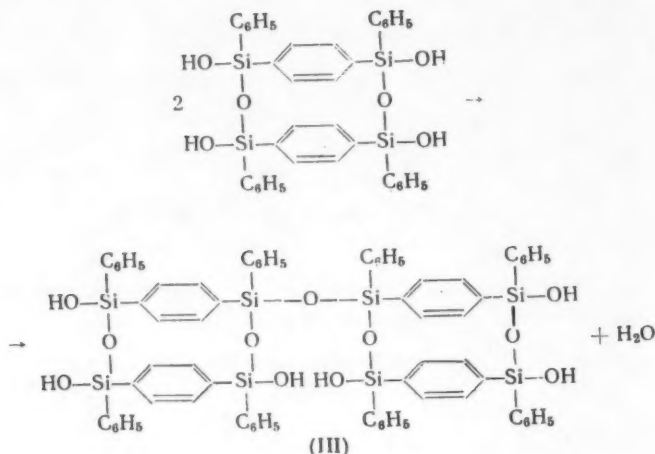
The infrared spectrum contained frequencies corresponding to the bonds $\text{C}_6\text{H}_5-\text{Si}$ (483, 473, 1124 and 1421 cm$^{-1}$); $-\diagup\!\!\!\diagdown\!-$ (545 and 1140 cm$^{-1}$); HO$-$Si (850-900, ~3400 and 3680 cm$^{-1}$); the vibration frequencies of the Si$-$O$-$Si bonds lay in the region 1015-1080 cm$^{-1}$. The Si$-$O$-$Si absorption band at 1080 cm$^{-1}$ in the spectrum of (II) had one maximum, whereas in the spectrum of (III) the most intense Si$-$O$-$Si band lay in the range 1015-1080 cm$^{-1}$. The proportion of hydroxy groups in (III) was less than in (II).

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## EXPERIMENTAL

Preparation of the Linear Compound. A hydrolysis apparatus was charged with 256.4 g (0.7 mole) of 1-(chloromethylphenylsilyl)-4-(dichlorophenylsilyl)benzene and 700 ml of ether, and hydrolysis was carried out with water at 18-25°. The duration of the hydrolysis was three hours. The ethereal solution was washed with water until neutral and filtered. Removal of ether left gleaming white crystals. We obtained 235.2 g (99.1%) of a substance, m.p. 84-85°, corresponding to the formula:

$$\text{HO}-\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{Si}}-\text{C}_6\text{H}_4-\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{Si}}-\text{O}-\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{Si}}-\text{C}_6\text{H}_4-\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{Si}}-\text{O}-\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{Si}}-\text{C}_6\text{H}_4-$$

$$-\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{Si}}-\text{O}-\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{Si}}-\text{C}_6\text{H}_4-\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{Si}}-\text{OH}$$
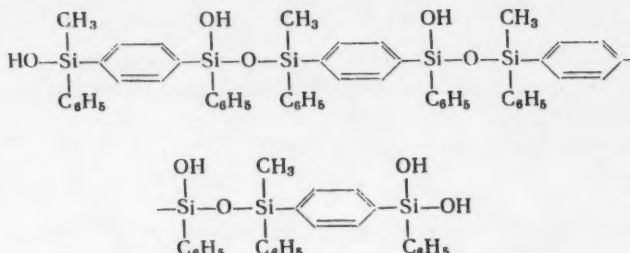
The substance was purified by two reprecipitations from carbon tetrachloride solution with petroleum ether (2.5 g of the substance was dissolved in 4 ml of carbon tetrachloride, and 10 ml of petroleum ether was added).

We did not establish the positions of the groups in this compound. Found: C 67.34, 67.41; H 5.38, 5.35; Si 16.37, 16.20; OH 7.52, 7.60%; mol. wt. 1305, 1353. $C_{76}H_{74}Si_8O_9$. Calculated: C 67.31; H 5.50; Si 16.57; OH 7.52%; mol. wt. 1356.

Preparation of Cyclic Phenylenebis(hydroxyphenylsilyl) Dioxide. The hydrolysis apparatus was charged with 428.3 g (1 mole) of p-bis(dichlorophenylsilyl)benzene and 1300 ml of ether. The hydrolysis and subsequent treatment were carried out under the conditions indicated for the preparation of the linear compound. We obtained 281 g (83.5%) of a substance corresponding to a cyclic phenylenebis(hydroxyphenylsilyl) dioxide. Found: C 64.20, 64.28; H 4.74, 4.86; Si 16.87, 16.80%; mol. wt. (in dioxane) 681, 682. $C_{36}H_{32}Si_4O_6$. Calculated: C 64.25; H 4.79; Si 16.70%; mol. wt. 673.

Preparation of the Bisheterocycle from Cyclic Phenylenebis(hydroxyphenylsilyl) Dioxide. Toluene-ether solutions of 50% strength, or solutions of greater strength in ether only, were prepared of the cyclic phenylenebis-(hydroxyphenylsilyl) dioxide and kept for 4-6 months, after which condensation to the bisheterocycle had occurred. Found: C 65.37, 65.60; H 4.74, 4.87; Si 16.51, 16.44%. $C_{72}H_{62}Si_8O_{11}$. Calculated: C 61.12; H 4.70; Si 16.93%.

## SUMMARY

1. A linear organosilicon compound with a phenylenesiloxane chain and a cyclic phenylenebis(hydroxyphenylsilyl) dioxide was synthesized.

2. A bisheterocyclic compound was isolated.

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# SPECTROSCOPIC INVESTIGATION OF THE EFFECT OF A SILICON ATOM ON DOUBLE BONDS IN ORGANOSILICON MOLECULES

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In our previous investigations on the physical and chemical properties of organosilicon compounds containing double bonds (C = C or aromatic) in different positions with respect to the silicon atom [1, 2] it was found that a silicon atom in the β-position to such a bond disturbs its electron environment, which leads, on the one hand, to increase in the reactivities of the corresponding compounds in electrophilic-substitution reactions and, on the other, to increase in the intensities of lines in the Raman spectrum, to bathochromic shifts in the ultraviolet spectrum, and to the occurrence of exaltation of $MR_D$.

In the present investigation this study was continued for the case of some p-disubstituted benzenes with the silicon atom in the β- or γ-position with respect to the aromatic ring. We determined the Raman spectra of the following compounds:



$$(CH_3)_3Si—CH_2—\langle\text{benzene}\rangle—Si(CH_3)_3; \qquad (I)$$

$$(C_2H_5)_3Si—CH_2—\langle\text{benzene}\rangle—Si(CH_3)_3; \qquad (II)$$

$$(CH_3)_3Si—CH_2—CH_2—\langle\text{benzene}\rangle—Si(CH_3)_3; \qquad (III)$$

$$(C_2H_5)_3Si—CH_2—CH_2—\langle\text{benzene}\rangle—Si(CH_3)_3; \qquad (IV)$$

$$(CH_3)_3Si—CH_2—\langle\text{benzene}\rangle—C\overset{O}{\underset{CH_3}{}}; \qquad (V)$$

$$(CH_3)_3Si—CH_2—CH_2—\langle\text{benzene}\rangle—C\overset{O}{\underset{CH_3}{}}, \qquad (VI)$$
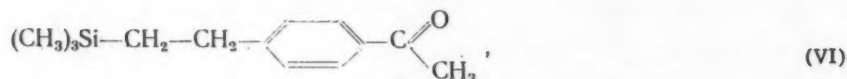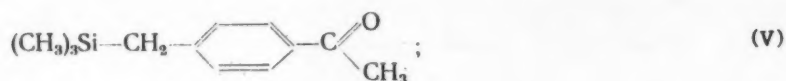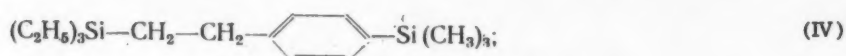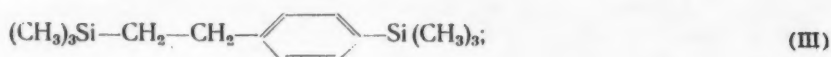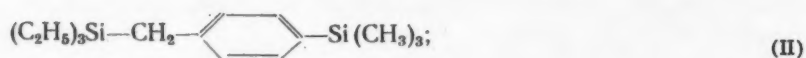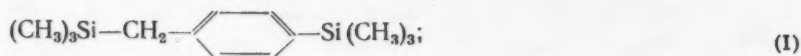
We determined the ultraviolet absorption spectra of (I), (III), (V), and (VI) and also of compounds with the silicon atom in the α-position with respect to the ring:

$$(CH_3)_3C—\langle\text{benzene}\rangle—Si(CH_3)_3 \qquad (VII)$$

$$(CH_3)_3Si—\langle\text{benzene}\rangle—C\overset{O}{\underset{CH_3}{}} \qquad (VIII)$$

The syntheses of the compounds investigated are described below. The Raman spectra were determined with an ISP-51 apparatus with a central camera by the usual method [3]. The intensities of the lines were measured photometrically at their maxima and expressed on the cyclohexane scale by the internal-standard method (we used $CCl_4$ as internal standard).

## Raman Spectra ($\Delta \nu$ in cm$^{-1}$)

$(CH_3)_3Si-CH_2-$ ⟨⟩ $-Si(CH_3)_3$ (I). 166 (15b), 236 (10b), 335 (25), 375 (5), 509 (15), 609 (245), 644 (25), 700 (30b), 764 (12b), 819 (25 sh), 849 (10b), 1029 (2), 1110 (120), 1157 (55), 1192 (50), 1217 (70), 1249 (10), 1317 (5), 1412 (20b), 1601 (200), 2896 (85b), 2956 (65b), 3014 (5), 3040 (2).

$(C_2H_5)_3Si-CH_2-$ ⟨⟩ $-Si(CH_3)_3$ (II). 150 (2), 215 (20b), 318 (2), 339 (2), 510 (5), 569 (20), 605 (50), 638 (20b), 698 (8), 727 (2), 753 (10), 825 (12), 980 (10 b), 1017 (8b), 1060 (7), 1113 (100), 1159 (45), 1196 (40), 1219 (60), 1261 (8), 1321 (2), 1360 (2), 1383 (0), 1420 (25b), 1463 (25b), 1601 (165), 2880-2907 (90 band), 2962 (75), 3023 (5), 3040 (2).

$(CH_3)_3Si-CH_2-CH_2-$ ⟨⟩ $-Si(CH_3)_3$ (III). 149 (15b), 171 (15), 207 (25b), 290 (10), 353 (5), 572 (2), 595 (120), 613 (2), 642 (18), 657 (10 sh), 698 (25b), 763 (5b), 809 (15), 851 (8b), 866 (5), 1000 (5), 1110 (45), 1193 (18), 1212 (7), 1251 (8b), 1275 (2), 1315 (5), 1415 (18), 1448 (5), 1600 (55), 2894 (75b), 2953 (60b), 3015 (3), 3070 (3).

$(C_2H_5)_3Si-CH_2-CH_2-$ ⟨⟩ $-Si(CH_3)_3$ (IV). 211 (20b), 301 (2), 360 (2), 520 (5), 567 (35b), 608 (16), 627 (8), 643 (25), 701 (12), 768 (18), 812 (16), 851 (10b), 900 (5), 980 (10), 1016 (12b), 1110 (40), 1134 (5), 1195 (16), 1212 (6), 1230 (2), 1319 (5), 1383 (2), 1420 (30b), 1466 (25b), 1601 (45), 2882 (60b), 2903 (60b), 2934 (7), 2916 (45), 3014 (2), 3046 (5).

$(CH_3)_3Si-CH_2-$ ⟨⟩ $-C\overset{O}{\underset{CH_3}{\diagdown}}$ (V). 178 (50b), 241 (35), 290 (100), 405 (30), 568 (10), 591 (160), 604 (180), 638 (160), 708 (125 b, db), 732 (20), 829 (50b), 860 (100), 954 (80), 1072 (450), 1154 (500), 1184 (400 sh), 1217 (675), 1272 (200), 1313 (10), 1359 (10), 1418 (35b), 1600 (1725), 1684 (515), 2897 (90), 2925 (40), 2956 (75), 3001 (25), 3060 (40).

$(CH_3)_3Si-CH_2-CH_2-$ ⟨⟩ $-C\overset{O}{\underset{CH_3}{\diagdown}}$ (VI).* 198 (w), 244 (w), 262 (w), 612 (160), 635 (140), 695 (100), 810 (w), 872 (w), 956 (w), 1077 (230), 1184 (180), 1207 (95), 1272 (120), 1326 (w), 1413 (w), 1610 (600), 1685 (260), 2900 (55, band), 2960 (70), 3060 (w).

The ultraviolet absorption spectra were determined with an SF-4 spectrophotometer in isooctane solution. The spectra are shown in Figures 1 and 2.

Comparison of the Raman spectra of (I), (II), and (V) ($\beta$-position of one Si with respect to the ring) with the spectra of (III), (IV), and (VI) ($\gamma$-position of Si with respect to the ring) shows quite clearly the sharp increase in the intensities of some lines in the spectra of (I), (II), and (V). We encountered an analogous phenomenon in [2] in a study of the Raman spectra of substances of the type ⟨⟩ $-$ $(CH_2)_n$ $-$ $SiR_3$ ($n = 0, 1$, and 2). It was then found that the most sensitive with respect to intensity were the lines corresponding to the symmetrical vibrations arising from the $E_g$-type vibrations of benzene. For p-disubstituted benzenes $X-$ ⟨⟩ $-(CH_2)_n-SiR_3$ this is also correct, i.e., maximum change in intensity is still shown by lines corresponding to symmetrical vibrations arising from $E_g^+$-type vibrations of benzene on lowering of the molecular symmetry from $D_{6h}$ to $C_{2v}$. Here we are concerned with the lines at 1605 cm$^{-1}$ ($\nu_{C-C}$ of the ring) and at 1190 cm$^{-1}$ (symmetrical deformational vibration of the ring) and also with two intense lines in the range 1000-1250 cm$^{-1}$, which, according to the work of Kohlrausch and his school [4, 5], correspond to symmetrical pulsational vibrations of the ring, one arising from predominant change in $C_{ar}-X$ and the

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*The spectrum of (VI) is incomplete; we succeeded in measuring intensities photometrically only for the brightest lines.
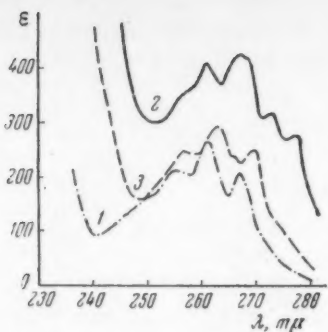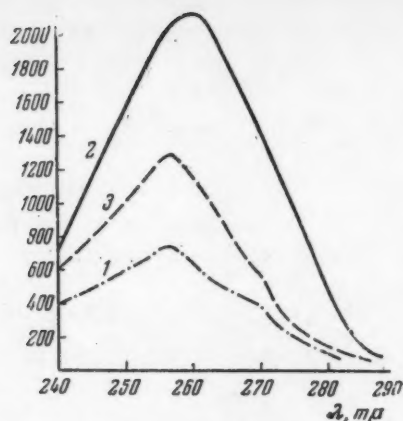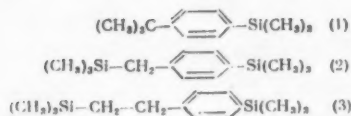
Fig. 1. Ultraviolet absorption spectra of:

$$(CH_3)_3C-\langle=\rangle-Si(CH_3)_3 \quad (1)$$

$$(CH_3)_3Si-CH_2-\langle=\rangle-Si(CH_3)_3 \quad (2)$$

$$(CH_3)_3Si-CH_2-CH_2-\langle=\rangle-Si(CH_3)_3 \quad (3)$$



Fig. 2. Ultraviolet absorption spectra of:

$$(CH_3)_3Si-\langle=\rangle-C\overset{O}{\underset{CH_3}{}} \quad (1)$$

$$(CH_3)_3Si-CH_2-\langle=\rangle-C\overset{O}{\underset{CH_3}{}} \quad (2)$$

$$(CH_3)_3Si-CH_2-CH_2-\langle=\rangle-C\overset{O}{\underset{CH_3}{}} \quad (3)$$
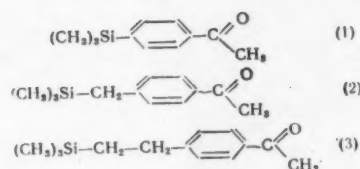
other from change in $C_{ar}-C\langle$ . These frequencies ($\underline{e}$ and e' in Kohlrausch's nomenclature) are readily identified in the spectrum because their magnitudes are very close to those observed for the corresponding monosubstituted benzenes. In our spectra the line 1215 cm$^{-1}$ (compare the line 1211 cm$^{-1}$ to toluene) corresponds to the frequency $\underline{e}$, and in the spectra of (I)-(IV) the line 1110 cm$^{-1}$ ( for $\langle=\rangle$ —Si(CH$_3$)$_3$ it is 1117 cm$^{-1}$) and in the spectra of (V)-(VI) the line 1072 cm$^{-1}$ (as for acetophenone) correspond to the frequency $\underline{e}'$.

The intensities of these lines, and also of the line 1684 cm$^{-1}$ in the spectra of (V) and (VI) ($\nu_{C=O}$) are compared in Table 1. The intensities were measured at the maxima of the lines* and were calculated for a given constant number of molecules in scattering volume.

Unlike the lines given in Table 1, those corresponding to antisymmetrical vibrations of the aromatic ring and internal vibrations of the (CH$_3$)$_3$Si group change little in intensity as we pass from compounds with the silicon atom in the β-position with respect to the ring to compounds with the silicon in the γ-position. Thus, the intensity of the line at about 640 cm$^{-1}$ (antisymmetrical deformational vibration of the ring) is 50 units in the spectrum of (I) and 45 units in the spectrum of (III).

In the spectra of compounds in which there is silicon in the β-position with respect to the ring there is a very intense line at 1150 cm$^{-1}$, which is absent in the spectra of (III), (IV), and (VI). The appearance of this line in the spectra of all alkenylsilanes in which the silicon is β with respect to the double bond was noted previously [6]. The intensities of the characteristic lines do not depend on the kind of group attached to silicon [in the present case change from methyl to ethyl as we pass from (I) to (II) and from (III) to (IV)]. Examples are given in Table 2. This is not a new phenomenon in the spectra of organosilicon compounds and was already met in the early work of Egorov [3, 7].

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*We took account of the fact that only the integral intensity of the line has physical meaning, but in the present case comparison of intensities at the maximum was justified in view of the almost identical half-widths of the lines compared. Thus, the measured integral intensity of the line 1605 cm$^{-1}$ of the compound

$$(CH_3)_3Si-(CH_2)_n-\langle=\rangle-C\overset{O}{\underset{CH_3}{}} ,$$
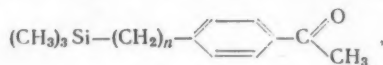
was found to be 9000 units for n = 1 (V) and 5000 units for n = 2 (VI), i.e., varied to approximately the same extent as the intensity at the maximum (Table 1).

## TABLE 1

Intensities of Some Characteristic Lines in the Spectra of p-Dibustituted Benzenes

| Frequency (cm$^{-1}$) | Intensity in the spectrum of $(CH_3)_3 Si - (CH_2)_n$ [benzene] $-X$ | | | | | Assignment |
|---|---|---|---|---|---|---|
| | X | Si(CH$_3$)$_3$ | | $-C(=O)CH_3$ | | |
| | n | 1 (I) | 2 (III) | 1 (V) | 2 (VI) | |
| 1110 | 250 | 100 | — | — | Symm. pulsational vibration of ring associated with change in the $C_{ar}-X$ coordinate |
| 1072 | — | — | 760 | 410 | |
| 1217 | 150 | 20 | 1140 | 175 | The same, but with change in the $C_{ar}-C\equiv$ coordinate |
| 1605 | 430 | 120 | 2900 | 1050 | $\nu_{C=C}$ of ring |
| 1190 | 105 | 40 | 680 | 325 | Symm. $\delta_{C=O}$ |
| 1684 | — | — | 860 | 475 | $\nu_{C=O}$ |

## TABLE 2

Intensities of Some Lines in the Spectra of Aryl-silanes (calculated for equal numbers of molecules in the scattering volume)
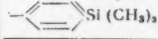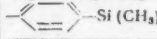
| Frequency (cm$^{-1}$) | Intensity in the spectrum of $R_3Si-CH_2-$[benzene]$-Si(CH_3)_3$ | | Frequency (cm$^{-1}$) | Intensity in the spectrum of $R_3Si-CH_2-CH_2-$[benzene]$-Si(CH_3)_3$ | |
|---|---|---|---|---|---|
| | R=CH$_3$ | R=C$_2$H$_5$ | | R=CH$_3$ | R=C$_2$H$_5$ |
| 644 | 50 | 52 | 642 | 40 | 55 |
| 1110 | 250· | 260 | 1110 | 100 | 100 |
| 1157 | 115 | 115 | | | |
| 1193 | 105 | 100 | 1193 | 40 | 40 |
| 1217 | 150 | 155 | 1212 | 15 | 15 |
| 1601 | 430 | 425 | 1600 | 120 | 115 |

Figure 1 shows that ultraviolet absorption spectra of (I), (II), and (VII), and Fig. 2 those of (V), (VI), and (VIII). For comparison with (I) and (III) we intentionally chose $(CH_3)_3C-$ [benzene] $-Si(CH_3)_3$ rather than $(CH_3)_3Si-$ [benzene] $Si(CH_3)_3$ since the aromatic ring is directly linked with two silicon atoms in the molecule of p-bis-trimethylsilylbenzene and this may lead to qualitatively new phenomena, in relation to (I) and (III), due to the effect of the second silicon atom on the ring. In the molecule of 1-t-butyl-4-(trimethylsilyl)benzene, which belongs to the same symmetry type as p-bistrimethylsilylbenzene, the ring is linked directly with one C atom and one Si atom as in compounds (I), and (III).
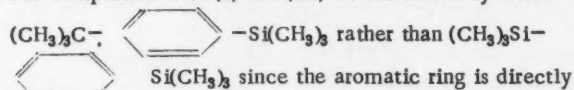
From an examination of the ultraviolet spectra it may be concluded that for compounds with a silicon atom $\beta$ to the aromatic ring the intensity of the bands is somewhat greater than for the $\alpha$- and $\gamma$-compounds, but the absorption maximum is displaced toward the long-wave region. We observed a similar phenomenon previously [2] for the series $(CH_3)_3Si(CH_2)_n-$ [benzene] ($n = 0, 1,$ and 2).

Finally, we may cite values of molecular refraction for organosilicon monosubstituted and p-disubstituted benzenes, both for those that we have studied spectroscopically and for the new $(CH_3)_3Si-(CH_2)_n$ [benzene] $-NO_2$ (Table 3). It must be remembered, of course, that in aromatic compounds exaltation of refraction is observed in the great majority of cases and the character of its change has received little study. Nevertheless, an examination of Table 3 shows that for compounds in which silicon is $\beta$ to the ring the exaltation of $MR_D$ ($\Delta$) is higher than in the case of the $\alpha$- and $\gamma$-compounds.
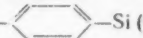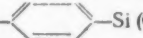
Anomalies of a chemical nature are also observed in compounds with silicon in the $\beta$-position with respect to the aromatic ring. Thus, Chernyshev, Dolgaya, and Petrov [8] studied the nitration of sila-hydrocarbons of the series $R_3Si-(CH_2)_n-$ [benzene]. It was found that, if the reactivity of the aromatic ring in this reaction was taken as unity for benzene, then for trimethylphenylsilane ($n = 0$) it was 1.64, for benzyltrimethylsilane ($n = 1$) it was 77.2, and for trimethylphenethylsilane ($n = 2$) it was 8.87. Such a variation in reactivity in the series investigated ($\beta \gg \gamma > \alpha$) cannot be explained except by the induction effect of the trimethylsilyl group.

TABLE 3

Molecular Refractions of Aryl- and Aralkyl-silanes

| Type of compound | n = 0 | | | n = 1 | | | n = 2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $MR_D$ found | $MR_D$ calcd. | Δ | $MR_D$ found | $MR_D$ calcd. | Δ | $MR_D$ found | $MR_D$ calcd. | Δ |
| $CH_3)_3Si—(CH_2)_n—$⟨benzene⟩ | 49,99 | 49,95 | 0,04 | 54,98 | 54,52 | 0,46 | 59,22 | 59,15 | 0,07 |
| $C_2H_5)_3Si—(CH_2)_n—$⟨benzene⟩ | 63,62 | 63,48 | 0,14 | 68,38 | 68,05 | 0,33 | 72,55 | 72,08 | 0,13 |
| $CH_3)_3Si—(CH_2)_n—$⟨benzene⟩$—C(=O)CH_3$ | 60,30 | 59,87 | 0,43 | 65,79 | 63,78 | 2,01 | 69,49 | 68,41 | 1,08 |
| $(CH_3)_3Si—(CH_2)_n—$⟨benzene⟩$—NO_2$ | 56,30 | 56,34 | 0,04 | 61,59 | 60,90 | 0,69 | — | — | — |
| $(CH_3)_3Si—(CH_2)_n—$⟨benzene⟩$—Si(CH_3)_3$ | — | — | — | 78,74 | 78,47 | 0,27 | 83,05 | 83,12 | 0,07 |
| $C_2H_5)_3Si—(CH_2)_n—$⟨benzene⟩$—Si(CH_3)_3$ | — | — | — | 92,30 | 91,74 | 0,56 | 95,49 | 95,22 | 0,27 |

The variation in the reactivity of aryl- and aralkyl-silanes under the action of nucleophilic reagents was studied for the case of the reaction of bromo compounds of the series $R_3Si—(CH_2)_n—$⟨benzene⟩$—Br$ with piperidine [9]. In this case the reactivity fell in the order $\alpha > \gamma > \beta$. Compounds in which the silicon atom was in the $\beta$-position with respect to the aromatic ring again showed anomalous reactivity, but in contrast with the case of electrophilic-substitution reactions, the reactivity was lower than that of neighboring homologs.

Hence, the results obtained in the present work for p-disubstituted benzenes are analogous to those of previous investigations [1, 2] and enable us to draw the general conclusion that in the series:

$$R_3Si(CH_2)_n—CH=CH_2$$

$$R_3Si—(CH_2)_n—⟨benzene⟩$$

$$R_3Si—(CH_2)_n—⟨benzene⟩—Si(CH_3)_3$$

$$R_3Si—(CH_2)_n—⟨benzene⟩—C(=O)CH_3$$
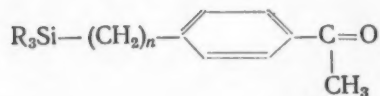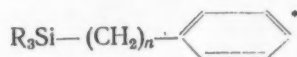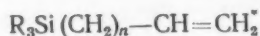
in which n = 0, 1, and 2, in the compounds for which n = 1, i.e., in which the double bond is in the $\beta$-position with respect to silicon, there are various anomalies in chemical and physical behavior: a) the reactivity varies anomalously; b) the intensities of the Raman lines corresponding to symmetrical vibrations of the system $Si—C—C=C$ or

$$Si—C—⟨benzene⟩,$$
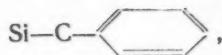
are increased; c) in the ultraviolet spectra there is a bathochromic shift of the absorption bands and an increase in their intensity; d) in most cases there is enhanced exaltation of molecular refraction. It is known that it is just such phenomena which are characteristic of compounds containing conjugated double bonds. Thus, Tatevskii and coworkers [10] in a study of the Raman spectra of dienes observed that as we pass from nonconjugated systems to conjugated systems the intensities of lines corresponding to the vibrations of $C=C$ bonds increase approximately tenfold

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* The complete Raman spectra of these compounds were given in [7].

# TABLE 4

Differences in Relative Increase of Intensity

| Type of compound | Intensities of lines | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $1600\,cm^{-1}\,(\nu_{C=C})$ | | | $1210\,cm^{-1}\,(e)$ | | | $1070{-}1110\,cm^{-1}\,(e')$ | | |
| | $I_{n=1}$ | $I_{n=2}$ | $K=\dfrac{I_{n=1}}{I_{n=2}}$ | $I_{n=1}$ | $I_{n=2}$ | $K=\dfrac{I_{n=1}}{I_{n=2}}$ | $I_{n=1}$ | $I_{n=2}$ | $K=\dfrac{I_{n=1}}{I_{n=2}}$ |
| $(CH_3)_3Si{-}(CH_2)_n{-}CH{=}CH_2$ | 180 | 95 | 1,9 | — | — | — | — | — | — |
| $(CH_3)_3Si{-}(CH_2)_n{-}\langle\!\!\!\bigcirc\!\!\!\rangle$ | 350 | 200 | 1,75 | 550 | 115 | 4,7 | — | — | — |
| $(CH_3)_3Si{-}(CH_2)_n\langle\!\!\!\bigcirc\!\!\!\rangle{-}Si(CH_3)_3$ | 430 | 120 | 3,6 | 150 | 20 | 7,5 | 250 | 100 | 2,5 |
| $(CH_3)_3Si{-}(CH_2)_n{-}\langle\!\!\!\bigcirc\!\!\!\rangle{-}C\!\!\stackrel{O}{\underset{CH_3}{<}}$ | 2900 | 1050 | 2,8 | 1140 | 170 | 6,7 | 760 | 410 | 1,9 |

and the intensity of the line at 1150 cm$^{-1}$ 25-fold on the average. Analogous results are reported in the papers of Shorygin and co-workers [11], Harrand and Martin [12], and, for systems containing the cyclopropane ring, Kazanskii, Aleksanyan, and others [13]. The increase in the intensity of the spectrum bonds is accompanied by the appearance of exaltation of MR$_D$ [14], a bathochromic shift of the absorption band (see e.g. [15]), and in some cases a parallel rise in reactivity.

Thus, there is a direct correspondence between our " β-effect" and the conjugation of double bonds. However, the effect observed for silanes is weakened about fivefold, for the intensity of the Raman lines of the double bonds increases only by a factor of 2-3 and the bathochromic shift does not exceed 5-7 m$\mu$.
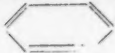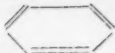
From the point of view of quantum mechanics the conjugation of double bonds is explained by the overlapping of $\pi$-electron orbitals. The " β effect" that we have observed cannot be explained in such a relatively graphic manner in that there are no $\pi$-electrons in the electron system of an Si$-$C bond. We consider that this effect is associated with the peculiar quantum-mechanical features of the structure of the electronic environment of an Si atom in the valence state. In particular, although silicon is in Group IV of the periodic system, it is almost unable to form double Si$=$C bonds, but, as it has unfilled 3d orbitals, it may be quinque- and sexa-valent in some compounds. On the basis of the analogy between our " β effect" and $\pi-\pi$ conjugation we may speak of a specific interaction between a double bond or aromatic ring and the structurally complex electronic environment of an Si atom in the valence state. It is quite probable that the occurrence of this effect is favored by the steric arrangement of the system Si$-$C$-$C$-$X, for which, as Stuart and Briegleb models show, a structure is possible in which the atoms 1 and 4

$$\underset{1\ \ \ 2\ \ \ 3\ \ \ 4}{}$$

are so close that overlapping of the van der Waals radii of these atoms occurs.

In conclusion, we must discuss the difference in the effect investigated for compounds of different series. If we examine the intensities of the line $\underline{e}$ (1210 cm$^{-1}$), $\underline{e}'$ (1070-1110 cm$^{-1}$), and the line corresponding to the vibration of the double bond (1600 cm$^{-1}$) it will be seen that for different types of compounds there are different relative increases in intensity as we pass from compounds for which $\underline{n}=2$ to compounds for which $\underline{n}=1$. If we assume that the relative increase in intensity K [equal to the ratio of the intensity of the appropriate line in the spectrum of the compounds for which $\underline{n}=1$ ($I_{n=1}$) to the intensity of the same line in the spectrum of the compound for which $\underline{n}=2$ ($I_{n=2}$), i.e., $K=\dfrac{I_{n=1}}{I_{n=2}}$ ] is a measure of the β effect, it may be shown (Table 4) that this effect diminishes along the series:

$$(CH_3)_3Si{-}CH_2{-}\langle\!\!\!\bigcirc\!\!\!\rangle{-}Si(CH_3)_3 > (CH_3)_3Si{-}CH_2{-}\langle\!\!\!\bigcirc\!\!\!\rangle{-}C\!\!\stackrel{O}{\underset{CH_3}{<}} >$$

$$> (CH_3)_3Si{-}CH_2{-}CH{=}CH_2 > (CH_3)_3Si{-}CH_2{-}\langle\!\!\!\bigcirc\!\!\!\rangle$$
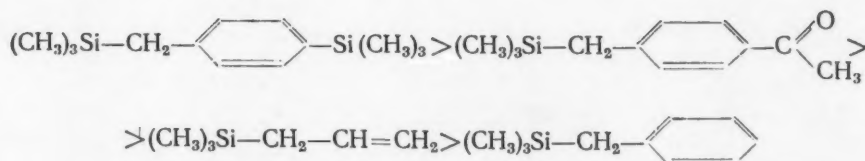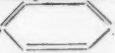
This question is too complex for us to reach any conclusions without further investigation both of line intensity (integral) and chemical properties. We may note only that the greater magnitude of the β effect for $(CH_3)_3Si-CH_2-$ ⬡ $-Si(CH_3)_3$ as compared with $(CH_3)_3Si-CH_2-$ ⬡ $-C\overset{O}{\underset{CH_3}{\diagdown}}$ is in accord with the theoretical calculations of Sanderson [16] on the distribution of electron density in the substituted aromatic ring. In particular, it follows from this work that the trimethylsilyl group has a greater tendency to drive electrons into the ring than the $-C\overset{O}{\underset{CH_3}{\diagdown}}$ group.

## EXPERIMENTAL

Preparation of 1-t-Butyl-4-(trimethylsilyl)benzene. 1-t-Butyl-4-(trimethylsilyl)benzene was synthesized from 1-chloro-4-t-butylbenzene and chlorotrimethylsilane by the Wurtz-Fittig reaction. The 1-chloro-4-t-butylbenzene used was prepared by the method of [17] and had the following properties: b.p. 110° (30 mm); $n^{20}D$ 1.5100; $d^{20}_4$ 1.0052; m.p. 24°.

A flask fitted with a sickle-shaped stirrer, a reflux condenser, and a dropping funnel was charged with 50 ml of toluene and 5 g of sodium. With vigorous stirring the molten sodium was broken down into fine globules in the boiling toluene. Stirring was continued while the contents of the flask were cooled, and the stirrer was then stopped and the toluene poured off. Dry ether (40 ml) was introduced into the flask together with 21 g (100% excess) of chlorotrimethylsilane; 16.8 g (0.1 mole) of 1-chloro-4-t-butylbenzene, as a solution in ether, was then added slowly over a period of one hour. The reaction mixture was heated with stirring for three hours further. The precipitate of NaCl was then filtered off, and ether and excess of chlorotrimethylsilane were distilled from the filtrate. Vacuum fractionation gave a fraction of b.p. 88-90° (5 mm). After two distillations over sodium we obtained 5.3 g (25.6%) of $(CH_3)_3Si$ ⬡ $C(CH_3)_3$, m.p. 78° (from ethanol).

Synthesis of 1-[(trialkylsilyl)methyl]-4-(trimethylsilyl)- and 1-[2-(trialkylsilyl)ethyl-4-(trimethylsilyl)-benzenes: Preparation of 2-(2-(triethylsilyl)ethyl]-4-(trimethylsilyl)benzene. $(C_2H_5)_3SiCH_2CH_2)$ ⬡ $C(CH_3)_3$ was prepared by the Grignard reaction. Slow addition was made of 20 g (0.185 mole) of chlorotrimethylsilane, at the temperature of boiling ether, to a Grignard reagent prepared from 40 g of 1-bromo-4-[2-(triethylsilyl)ethyl]benzene and 3.2 g (0.133 mole) of magnesium in 100 ml of ether. When the addition of the chlorotrimethylsilane was complete, the mixture was stirred for eight hours at the boiling point. The mixture was then decomposed in the usual way, and the organic layer was dried over calcium chloride. Fractionation gave: Fraction I (16 g), b.p. 90° (2.5 mm); this was

$$(C_2H_5)_3SiCH_2CH_2 ⬡ ; \quad n^{20}_D 1,4965; \quad d^{20}_4 0,8866.$$

Fraction II (6 g), b.p. 135-140° (3 mm). Two fractionations of Fraction II over sodium gave 4 g of $(C_2H_5)_3Si-CH_2-CH_2-$ ⬡ $-Si(CH_3)_3$. Its properties are given in Table 5.

We have noted previously the low reactivity of organomagnesium compounds of this type in an ether medium [18]. Therefore, with the object of raising the yield of 1-[2-(triethylsilyl)ethyl]-4-(trimethylsilyl)benzene the experiment was repeated at a higher temperature in a tetrahydrofuran medium. To the Grignard reagent prepared from 45 g of the bromo compound, 5 g of magnesium, and 120 ml of tetrahydrofuran we added 32 g of chlorotrimethylsilane at the boiling point of the medium. The contents of the flask were then boiled further for three hours. The mixture was decomposed, and the tetrahydrofuran layer was separated and dried over calcium chloride. Fractionation gave a fraction of b.p. 138-140° (3 mm), and by two distillations of this over sodium we obtained 33 g (78%) of

$$(C_2H_5)_3Si-CH_2-CH_2-$$
$$- ⬡ -Si(CH_3)_3;$$

The silicon-containing aromatic ketones were prepared by the method given in [19].

## SUMMARY

1. The Raman and ultraviolet absorption spectra were determined for some silicon-containing p-disubstituted benzenes.

2. Compounds in which the Si atom was in the $\beta$-position with respect to the ring were found to have anomalous reactivity as compared with compounds with the Si atom in the $\alpha$- or $\gamma$-position; there was an increased intensity of the Raman lines corresponding to symmetrical vibrations of the system $-\text{Si}-\text{C}-\!\!\!\diagdown\!\!\!-\!\!\!\diagup\!\!\!-X$ and also increased intensity and a bathochromic shift of the bands in the ultraviolet spectra; there was also increased exaltation of $MR_D$.

3. In the systems $-\text{Si}-\text{C}-\text{C}=\text{C}$ and $-\text{Si}-\text{C}-\!\!\!\diagdown\!\!\!-\!\!\!\diagup\!\!\!-X$ there is a specific mutual interaction between the double bond or aromatic ring and the structurally complex electronic environment of the Si atom in the valence state.

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TABLE 5

Properties and Yields of Silahydrocarbons Obtained

| Compound | Yield (%) | B.p. in °C (p in mm) | $n_D^{20}$ | $d_4^{20}$ | Calcd. (%) C | H | Si | Found (%) C | H | Si |
|---|---|---|---|---|---|---|---|---|---|---|
| (CH₃)₃Si—CH₂—⟨⟩—Si(CH₃)₃ | 84 | 85—86 (4) | 1,4911 | 0,8681 | 66,13 | 10,47 | 23,7 | 66,30 / 66,26 | 10,18 / 10,08 | 23,63 / 23,60 |
| (CH₃)₃Si—CH₂—CH₂—⟨⟩—Si(CH₃)₃ | 80 | 110—112 (5) | 1,4788 | 0,8668 | 67,25 | 10,4 | 22,35 | 67,30 / 67,22 | 10,62 / 10,43 | 22,31 / 22,59 |
| (C₂H₅)₃Si—CH₂—⟨⟩—Si(CH₃)₃ | 71 | 130—132 (6) | 1,4990 | 0,8842 | 69,05 | 10,79 | 20,16 | 69,12 / 68,88 | 10,71 / 10,77 | 20,11 |
| (C₂H₅)₃Si—CH₂—⟨⟩—CH₂—Si(CH₃)₃ | 78 | 139 (3) | 1,4939 | 0,8877 | 70,0 | 10,95 | 19,05 | 69,78 / 69,54 | 11,13 / 11,11 | 18,92 |

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# HAMMETT CONSTANTS OF SOME (TRIALKYLSILYL)ALKYL GROUPS

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The nature of the silyl group
$$R^2 - \underset{\underset{R^3}{|}}{\overset{\overset{R^1}{|}}{Si}} - B$$
largely determines the reactivity of a fourth silicon-attached group

$R^4$ in various reactions. As silicon is a more positive element than carbon (according to Pauling the electronegativity of carbon is 2.5 and that of silicon 1.8), in relation to carbon it should show electron-donating properties. However, the character of the silyl group is determined not only by the nature of the silicon atom, but also largely by the natures of the three atoms or groups $R^1$, $R^2$, and $R^3$ attached to it.

When $R^1$, $R^2$, and $R^3$ are alkyl groups, the silyl group is generally electron-donating. Thus, all trialkylsilyl-substituted aliphatic acids have been found to be weaker than the corresponding unsubstituted acids [1]. This view of the electron-donating character of trialkylsilyl groups was reached by Noll, Daubert, and Speier [2] and also by Sommer and Rockett [3] from the analysis of ionization constants of aliphatic silicon-containing amines. The dipole moments of various organosilicon compounds also support the view of the electron-donating properties of trialkylsilyl groups [4].

Unlike the trialkylsilyl group, the trichlorosilyl group is an electron acceptor. This view is supported, for example, by the extremely low reactivity of C−H bonds of the $\alpha$-carbon atoms of various alkyltrichlorosilanes in photochemical chlorination [5]. The electron-accepting character of the trichlorosilyl group followed also from the investigation of the competing bromination of an equimolecular mixture of trichlorophenylsilane and benzene [6].

The extent of the specific effect of a silicon atom on a double bond, aromatic ring, or another atom in the $\beta$-position is determined by the nature of the silyl group [6-11]. When the silicon atom is attached to three alkyl groups, this effect is very clearly marked, but when the silicon atom is attached to three chlorine atoms the effect of enhanced reactivity of $\beta$-functional groups is at a minimum. Alkyldichlorosilyl and dialkylchlorosilyl groups occupy intermediate positions.

Silyl groups are peculiar also in that in different compounds the same $R_3Si$ group may have opposite effects of different groups to which it is attached, depending on the natures of these groups. The dipole moments of p-(tri-methylsilyl)aniline [$\mu$ = 1.66 D; moment of $(CH_3)_3Si$ group −0.13 D], N,N-dimethyl-p-(trimethylsilyl)aniline [$\mu$ = 1.84 D; moment of $(CH_3)_3Si$ group −0.26 D] [4], and p-(trimethylsilyl)toluene [$\mu$ = 1.46 D; moment of $(CH_3)_3Si$ group = −0.06 D] [4] show that in these compounds the trimethylsilyl group is an electron acceptor.

The electron-accepting character of $(CH_3)_3Si$ and $(C_2H_5)_3Si$ groups follows also from the dissociation constants of p-(trimethylsilyl)- and p-(triethylsilyl)-benzoic acids (Table 1, Compounds 1 and 4) and the ionization constant of p-(trimethylsilyl)aniline (Table 2, Compound 1).

As the dipole moment of p-(trimethylsilyl)benzoic acid [$\mu$ = 1.29 D; moment of $(CH_3)_3Si$ group = +0.46 D] [4] indicates that the $(CH_3)_3Si$ group has an electron-donating character, it follows that in this compound the group is an electron acceptor only in the dynamic state.

The electron-accepting properties of trialkylsilyl groups in the acids and amines cited above are to be explained by the ability of a silicon atom to form supplementary bonds by the filling of its vacant 3d orbitals [4, 12-14]. As a

## TABLE 1

Apparent Dissociation Constants of Acids in 60% Aqueous Ethanol at 25°

| No. | Acid | Dissociation constant $K_a \cdot 10^5$ | Literature reference |
|---|---|---|---|
| 1 | $(CH_3)_3 SiC_6H_4COOH\text{-}p$ | 1,11 | [12] |
| 2 | $(CH_3)_3 SiCH_2C_6H_4COOH\text{-}p$ | 0,447; (0,464) | [12] |
| 3 | $(CH_3)_3 SiCH_2CH_2C_6H_4COOH\text{-}p$ | 0,59 | * |
| 4 | $(C_2H_5)_3 SiC_6H_4COOH\text{-}p$ | 1,13 | [12] |
| 5 | $(C_2H_5)_3 SiCH_2C_6H_4COOH\text{-}p$ | 0,47 | * |
| 6 | $(C_2H_5)_3 SiCH_2CH_2C_6H_4COOH\text{-}p$ | 0,63 | * |
| 7 | $C_6H_5COOH$ | 1,00 | * |
| 8 | $(CH_3)_3 CC_6H_4COOH\text{-}p$ | 0,70 | [12] |
| 9 | $(C_2H_5)_3 CC_6H_4COOH\text{-}p$ | 0,71 | [12] |

*$K_a$ was determined in the present investigation.

## TABLE 2

Ionization Constants of Aniline Hydrochlorides in 50% by Volume of Ethanol at 25°

| No. | Aniline (derivative) | Ionization constant $K_b \cdot 10^4$ | Literature reference |
|---|---|---|---|
| 1 | $(CH_3)_4 SiC_6H_4NH_2\text{-}p$ | 0,436** | [13] |
| 2 | $(CH_3)_3 SiC_6H_4NH_2\text{-}p$ | 0,229** | [13] |
| 3 | $(CH_3)_3 SiCH_2C_6H_4NH_2\text{-}p$ | 0,0815 | * |
| 4 | $(CH_3)_3 SiCH_2CH_2C_6H_4NH_2\text{-}p$ | 0,132 | * |
| 5 | $(CH_3)_3 SiCH_2CH_2CH_2C_6H_4NH_2\text{-}p$ | 0,166 | * |
| 6 | $(CH_3)_3 SiCH_2CH_2CH_2CH_2C_6H_4NH_2\text{-}p$ | 0,195 | * |
| 7 | $C_6H_5NH_2$ | 0,375 (0,24)** | [13]* |
| 8 | $CH_3C_6H_4NH_2\text{-}p$ | 0,115 | * |

*$K_b$ was determined in the present investigation
**$K_b$ was determined in aqueous solution.

result of this tendency there is a shift of the $\pi$-electrons of the aromatic ring toward the silicon atom even though trialkylsilyl groups are electron donors by nature.

In several of our investigations [6, 7, 11] and in those of Mironov [8-10] it was noted that the silicon atom has a specific effect on a double bond, aromatic ring, $C-Cl$ bond, or other bond in the 3,4-position in the system $\underset{1\ \ 2\ \ 3\ \ 4}{Si-C-C-X}$. These effects in the series of organosilicon compounds form one of the examples of similar phenomena characteristic for the systems $\underset{1\ \ 2\ \ 3\ \ 4}{Y-C-C-X}$. For organic compounds of mercury and tin and for various other organometallic compounds, such phenomena have been extensively studied by Nesmeyanov and co-workers [15].

The effect of the silyl group on the aromatic ring in trialkylbenzylsilanes shows itself in their enhanced reactivity (as compared to neighboring homologs) toward electrophilic reagents and their reduced reactivity toward nucleophilic reagents; also in their higher intensities of the characteristic frequencies of the aromatic ring in the Raman spectra and of the bands in the ultrasiolet spectra. Trialkylbenzylsilanes also have higher dipole moments than their close homologs. Unlike trialkylsilyl groups, (trialkylsilyl)methyl groups always behave as powerful electron-donating groups.

In the present paper we give a quantitative characterization of the nature of some (trialkylsilyl)alkyl groups by means of the values of their Hammett constants $\sigma$ and $\sigma^+$ [16, 17]. For the calculation of Hammett constants we determined the dissociation constants of a series of p-(trialkylsilylalkyl)-substituted aromatic acids (Table 1) and

the ionization constants of analogous amines (Table 2). The constants $\sigma$ and $\sigma^+$ calculated on this basis for a series of $R_3Si(CH_2)_n$ groups are given in Table 3. This table gives Hammett constants for the groups $(CH_3)_3Si$, $(C_2H_5)_3Si$, and $(C_6H_5)_3Si$ taken from the literature or calculated from data in the literature.

TABLE 3

Hammett Constants of Some Silyl Groups

| No. | Silyl group | $\sigma_{para}$ | $\sigma_{meta}$ | $\sigma^+_{para}$ | $\sigma^+_{meta}$ | Literature references |
|---|---|---|---|---|---|---|
| 1 | $(CH_3)_3Si$ | +0,023 | −0,080 | +0,09 | −0,040 | [12, 13, 18] |
| 2 | $(C_2H_5)_3Si$ | +0,028 | — | — | — | [12] |
| 3 | $(C_6H_5)_3Si$ | +0,095 | −0,030 | +0,29 | +0,10 | [19] |
| 4 | $(CH_3)_3SiCH_2$ | −0,256 | −0,205 | −0,22 | — | * [20] |
| 5 | $(C_2H_5)_3SiCH_2$ | −0,235 | — | — | — | * |
| 6 | $(CH_3)_3SiCH_2CH_2$ | −0,173 | — | −0,157 | — | * |
| 7 | $(C_2H_5)_3SiCH_2CH_2$ | −0,145 | — | — | — | * |
| 8 | $(CH_3)_3SiCH_2CH_2CH_2$ | — | — | −0,116 | — | * |
| 9 | $(CH_3)_3SiCH_2CH_2CH_2CH_2$ | — | — | −0,093 | — | * |

*The Hammett constants were determined in the present investigation.

An examination of the Hammett constants of the $(CH_3)_3Si$ and $(C_6H_5)_3Si$ groups shows that, since $\sigma_{meta}$ is negative in each case, both are electron donors. In the meta-position, of course, no displacement of electrons along the chain from one substituent to the other occurs. On the other hand, $\sigma_{para}$ of these groups, and also of $(C_2H_5)_3Si$, is positive, which indicates the apparent electron-accepting character of these groups arising from displacement of

electrons along the chain, namely $R_3Si$  $_X$ , due to the presence of vacant $\underline{d}$ orbitals in silicon. The occur-

rence of such displacement is supported also by the fact that the differences $\sigma_{para} - \sigma_{meta}$ and $\sigma^+_{para} - \sigma^+_{meta}$ for these silyl groups are positive.

Different relations are observed for the indication of a silicon atom with a $\beta$-functional group, double bond, or aromatic ring, as considered in the present paper. For benzyltrimethylsilane the difference $\sigma_{para} - \sigma_{meta}$ is −0.051. The negative sign of this difference shows that in this case there is no withdrawal of $\pi$-electrons of the aromatic ring to the silicon atom and, still more, to its d-orbitals. On the other hand the $(CH_3)_3SiCH_2$ group is strongly electron-donating, and it has a stronger effect in the para-position than in the meta-position. For the same group $\sigma^+_{para} - \sigma_{para} = +0.36$, i.e., this difference is of a magnitude that is outside the limits of experimental error. From these data the specific effect of a silyl group on an aromatic ring in the $\beta$-position to the silicon atom is clearly seen.

The determining influence of the nature of the remaining three silicon-attached atoms or groups on the magnitude of this effect, and also the specific behavior of $\beta$-functional organosilicon compounds known under the general name of the "$\beta$-effect", prompts the view that one of the main causes of so-called $\sigma-\sigma$ or $\sigma-\pi$ conjugation is the steric factor of the disposition of the silicon atom and the atom X in the system $\underset{1 \quad 2 \quad 3 \quad 4}{Si-C-C-X}$. An examination of Stuart-Briegleb models of various organosilicon compounds shows that the atom X in such a system may approach the silicon atom very closely with overlapping of van der Waals radii. Hence, through its electronic environment the silicon atom may have an appreciable effect on the 3,4-bond. Such bonds are strongly polarized, which results in reactivity that is anomalous with respect to neighboring homologs.

In this connection it is interesting to note that in the nitration of benzyltrimethylsilane with the general increase in activity of the aromatic ring in relation to benzene the highest reactivity is found in the ortho-position, i.e., at the C−H bond in the 3,4-position with respect to silicon; the partial rate factors for this case are $F_0 = 182$, $F_{meta} = \sim 0$, and $F_{para} = 49$ [11].

EXPERIMENTAL

We described the preparation of para-substituted silicon-containing benzoic acids and anilines previously [21].

The apparent dissociation constants of benzoic acids were determined by the potentiometric-titration method. A weighed amount of about 0.1 g of the silicon-substituted benzoic acid was dissolved in 100 g of aqueous ethanol (60% by weight) and titrated with 0.1 N NaOH ($CO_2$-free). The titration was carried out at 25 ± 0.1°. The hydrogen-ion concentration was measured with glass and saturated calomel electrodes with an LP-5 electron tube potentiometer. The value of pK was determined graphically as the point of 50% neutralization of the acid. The pK of benzoic acid was determined for comparison. The values of pK obtained are given in Table 4.

TABLE 4

pK Values for Benzoic and Various Organosilicon Acids

| No. | Formula of acid | pK | |
|-----|-----------------|------|------|
| 1 | $C_6H_5COOH$ | 6,0; | 6,0 |
| 2 | $(CH_3)_3SiCH_2C_6H_4COOH$-$p$ | 6,36; | 6,35 |
| 3 | $(CH_3)_3SiCH_2CH_2C_6H_4COOH$-$p$ | 6,25; | 6,23 |
| 4 | $(C_2H_5)_3SiCH_2C_6H_4COOH$-$p$ | 6,33; | 6,32 |
| 5 | $(C_2H_5)_3SiCH_2CH_2C_6H_4COOH$-$p$ | 6,2; | 6,2 |

The value of $\rho$ in Hammett's equation $\log k/k_0 = \sigma\rho$ for the given conditions, as determined by us and calculated from data in the liberature [12], was 1.38. The values of $\sigma$ obtained are given in Table 3.

For the determination of the ionization constants of anilines containing para-silicon-containing substituents, a weighed amount of about 0.1 g of the aniline hydrochloride was dissolved in 100 ml of aqueous ethanol (50% by volume) and titrated with 0.1 N NaOH ($CO_2$-free). Potentiometric titration was then carried out with the same electrodes and at the same temperature as in the determination of the dissociation constants of benzoic acids. Ionization constants were determined also for some aniline hydrochlorides that contained no silyl substituents. The values of pK obtained are given in Table 5.

TABLE 5

pK Values for Aniline, p-Toluidine, and Some Organosilicon Amines

| No. | Formula of aniline | pK |
|-----|--------------------|------|
| 1 | $C_6H_5NH_2$ | 4,43 |
| 2 | $p$-$CH_3C_6H_4NH_2$ | 4,94 |
| 3 | $p$-$(CH_3)_3SiCH_2C_6H_4NH_2$ | 5,09 |
| 4 | $p$-$(CH_3)_3SiCH_2CH_2C_6H_4NH_2$ | 4,90 |
| 5 | $p$-$(CH_3)_3SiCH_2CH_2CH_2C_6H_4NH_2$ | 4,78 |
| 6 | $p$-$(CH_3)_3SiCH_2CH_2CH_2CH_2C_6H_4NH_2$ | 4,71 |

The value of $\rho$ in Hammett's equation $\log k/k_0 = \sigma^+\rho$ for the given conditions, as found by us, was 3.0. Calculated values of $\sigma^+$ are given in Table 3.

## SUMMARY

1. The results confirm that in various phenylsilanes silicon can occur in the $Si^-$ (V) state on account of free 3d orbitals.

2. The specific effect of a silicon atom on $\beta$-functional groups is clearly determined by the specific character of the structure of these compounds together with the induction effects of the silyl and functional groups.

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# SYNTHETIC ANESTHETICS

## COMMUNICATION 33. 1,3,5-TRIMETHYL-4-PIPERIDONE AND SOME OF ITS DERIVATIVES*

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In a paper on the synthesis of 1,2,6-trimethyl-4-piperidone and its derivatives [1] the reason for the choice of symmetrically substituted piperidine derivatives for investigation has already been stated. In the present investigation such a substance, 1,3,5-trimethyl-4-piperidone (I), was taken for study. One possible route to this piperidone could be the ester condensation of 3-dimethylamino-2-methylpropionic ester (II), obtained by the addition of dimethylamine to methylacrylic ester, with subsequent decarboxylation and cyclization:
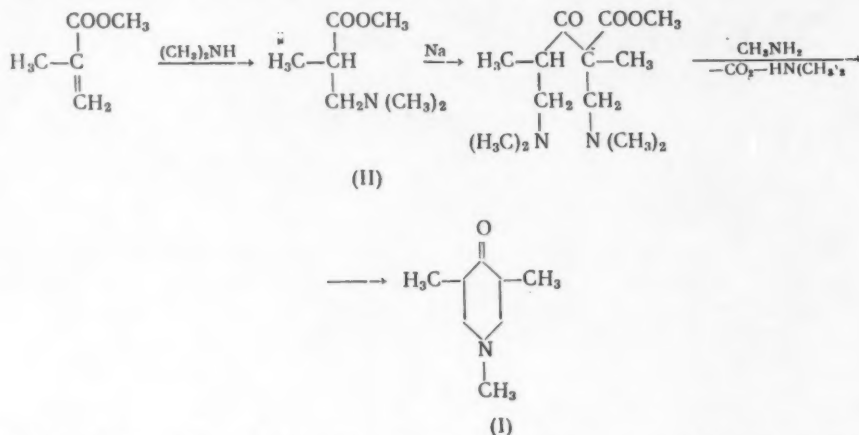


This route did not lead to the required result because at the condensation stage the pure reaction product was not obtained in a sufficiently good yield. We succeeded in obtaining the piperidone (I) by a different method based on the use of 2,4-dimethyl-3-pentanone as starting material:



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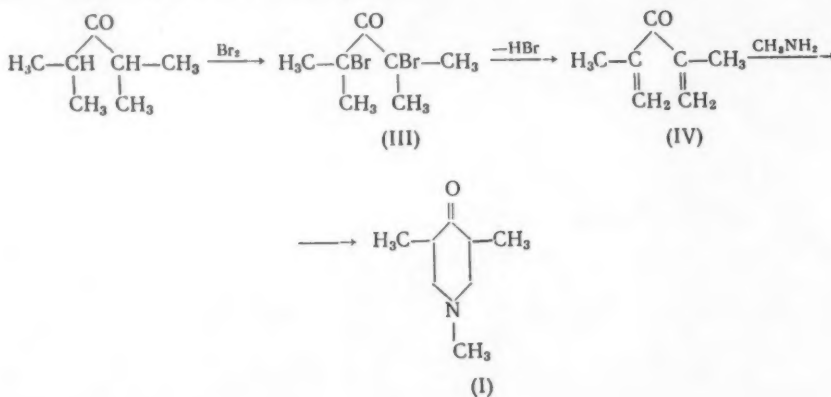
*The work was begun under the direction of I. N. Nazarov.

2,4-Dimethyl-2-pentanone, unlike ketones not containing substituents in both $\alpha$-positions which readily give dibromo derivatives in ethereal solution [2, 3] or in presence of water [4], forms only a monobromo derivative. The required dibromo-2,4-dimethyl-3-pentanone (III) we prepared by the bromination of 2,4-dimethyl-3-pentanone in presence of phosphorus, which is a simplification of the previously proposed method [5] of bromination with phosphorus pentabromide. The elimination of hydrogen bromide from (III) might be effected in several ways, which were checked. The first way consisted in the protection of the keto group as the ethylene ketal, elimination of hydrogen bromide with alkali, and hydrolysis with acid [6]. However, even under very severe conditions we did not succeed in effecting the protection of the CO group of the ketone.

The second way consisted in the replacement of bromine by the acetoxy group and subsequent pyrolysis of the diacetate [7]. This way also was found to be inadmissable. Despite variation in the conditions of carrying out the reaction of the dibromo ketone with potassium acetate, the products were mixtures of various substances, generally containing halogen.

The third way consisted in the direct dehydrobromination of the dibromo ketone. The use of N,N-diethyl-aniline did not give a satisfactory result. The use of lithium bromide in N,N-dimethylformamide [8] enabled us to obtain 2,4-dimethyl-3-pentadienone (IV) in moderate yield but not in a completely pure state. Another disadvantage of this method was the large consumption of lithium bromide (6 moles per mole of dibromo ketone). The best results were obtained by the joint action of N,N-diethylaniline and relatively small amounts of lithium bromide at about 150° with simultaneous distillation of the product from the reaction mixture. The 2,4-dimethyl-3-penta-dienone (IV) so obtained was fairly pure, and its structure was confirmed by the ultraviolet absorption spectrum of the 2,4-dinitrophenylhydrazone and by hydrogenation to the original 2,4-dimethyl-3-pentanone.

Reaction of 2,4-dimethyl-3-pentadienone (IV) with aqueous-methanolic methylamine gave a 90% yield of the required 1,3,5-trimethyl-4-piperidone (I), the hydrochloride of which reacted with excess of phenyllithium and formed a mixture of the isomeric 1,3,5-trimethyl-4-phenyl-4-piperidinols (V$\alpha$) and (V$\beta$):
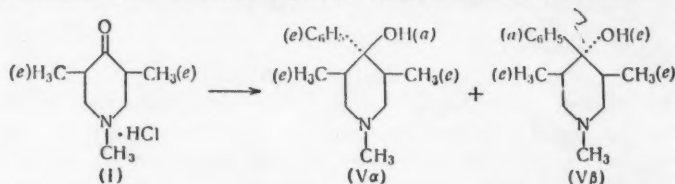


In this mixture the $\alpha$-isomer of the phenylpiperidinol(V$\alpha$) was predominant; the $\beta$-isomer (V$\beta$) was formed in only about one-twentieth the amount. It is probable that in the hydrochloride of the piperidone (I) the methyl groups occupy the energetically more favored diequatorial (cis) position, and in the phenyllithium synthesis there is preferential formation of the alcohol with the phenyl group also in the equatorial position, i.e., the $\alpha$-isomer. The simultaneous formation of the epimeric alcohol, the $\beta$-isomer with the phenyl group in the axial position, is also possible.

The action of phenyllithium on the piperidone (I) base also led to the formation of a mixture of isomeric alcohols. Apart from the $\alpha$-isomer of the phenylpiperidinol (V$\alpha$) we succeeded in isolating the third theoretically possible $\gamma$-isomer (V$\gamma$), the amount of which was about one-sixth of the amount of the $\alpha$-isomer:
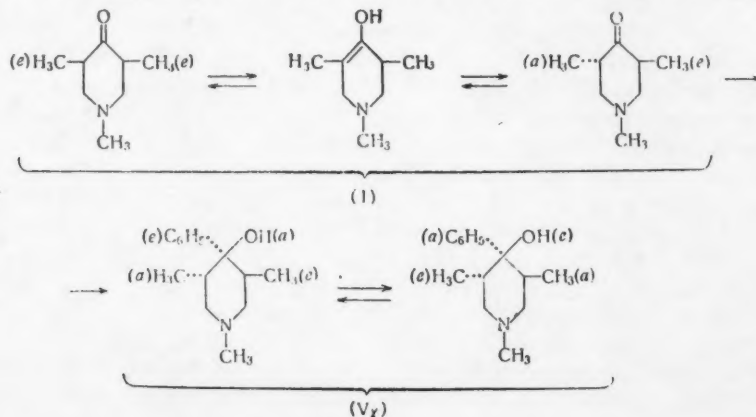
It is evident that the piperidone (I) base consists of an equilibrium mixture of both possible forms with a predominance of the diequatorial cis form. The small amount of trans form must lead to the formation of the γ -isomer of the phenylpiperidinol (Vγ), which is a racemic alcohol containing the phenyl group in the equatorial position, but permitting of an extremely probable conversion form with an axial phenyl group. The results that we obtained on the ability of these isomeric alcohols to be esterified under the action of propionyl chloride are in good accord with the above considerations. Thus, the β-isomer of the phenylpiperidinol (Vβ), which contains a hydroxyl group in the equatorial position, forms a propionic ester hydrochloride already after a single treatment with propionyl chloride. The γ -isomer (Vγ), which can be esterified only in its conversion form with an equatorial hydroxyl, requires three treatments with propionyl chloride to give complete reaction. Finally, the α-isomer (Vα), which contains an axial hydroxyl, is largely recovered unchanged after two treatments with propionyl chloride. We succeeded in esterifying the α-isomer only after heating it with propionic anhydride in presence of pyridine.

Tests of analgesic activity in Professor M. D. Mashkovskii's laboratory (VNIKhFI) showed that activity (equal to to that of promedol) was present only in the γ -phenylpiperidinol propionic ester hydrochloride. The absence of activity in the hydrochlorides of the propionic esters of the α- and β-isomers corresponds to the results obtained earlier for derivatives of cis-1,2,6-trimethyl-4-piperidinol [1], and to some extent it supports the view that in these isomers there is a cis configuration of methyl groups.

## EXPERIMENTAL

Preparation of 2,4-Dibromo-2,4-dimethyl-3-pentanone (III). With stirring and heating to 65-70° slow addition was made of 816 g (5.1 moles) of bromine to a mixture of 282 g (2.47 moles) of 2,4-dimethyl-3-pentanone (b.p. 123-125°; $n^{20}D$ 1.4015) and 3.1 g of red phosphorus. The mixture was then heated at 95° until hydrogen bromide ceased to be liberated (one hour). When the mixture was cool, the excess of bromine was removed by addition of $Na_2SO_3$ solution, the mixture was neutralized with sodium carbonate solution, the reaction product was separated, the aqueous layer was extracted with chloroform, and the combined extracts were dried with calcium chloride. Vacuum distillation gave 539 g (80.2%) of 2,4-dibromo-2,4-dimethyl-3-pentanone (III), b.p. 92-95° (15 mm) and $n^{20}D$ 1.5058.

Dehydrobromination of 2,4-Dibromo-2,4-dimethyl-3-pentanone. a) A mixture of 27.2 g (0.1 mole) of 2,4-dibromo-2,4-dimethyl-3-pentanone and 44.7 g (0.3 mole) of N,N-diethylaniline was heated in a vacuum (about 100 mm) at 150-160°. No distillation of product was observed. When cool, the partially crystallized mass was diluted with ether, and the precipitate of N,N-diethylaniline hydrobromide was filtered off. The precipitate weighed 26 g (50% of the expected amount). After distillation of the filtrate we isolated 2.4 g of a liquid containing halogen which darkened in color; b.p. 61-73° (80 mm).

b) A mixture of 13.6 g (0.05 mole) of the dibromodimethylpentanone, 22.4 g (0.15 mole) of N,N-diethylaniline, and 35 ml of methanol was refluxed for 18 hours. When cool, the mixture was diluted with ether, when a very small amount of N,N-diethylaniline hydrobromide was precipitated.

c) A mixture of 13.6 g (0.05 mole) of the dibromodimethylpentanone, 26.1 g (0.3 mole) of fused lithium bromide, and 46 ml of N,N-dimethylformamide was heated in a nitrogen atmosphere for three hours at 90-100°. When cool, the mixture was diluted with 100 ml of water and extracted with ether. Distillation of the extract gave 2.7 g of a substance of b.p. 52-52.5° (15 mm) and $n_D^{19.5}$ 1.4410. Halogen was absent.

d) A mixture of 539 g of the dibromodimethylpentanone, 800 ml of N,N-dimethylaniline, and 65 g of ground anhydrous LiBr was placed in a three-necked flask fitted with thermometer, capillary for the passage of nitrogen, a Vigreux column, and a condenser set for distillation. With the aid of a manostat a pressure of 110 mm was established in the system, and the reaction mixture was heated slowly until reaction set in (147°). As 2,4-dimethyl-3-pentadienone accumulated in the reaction mixture the temperature in the latter fell (to 118°) and unsaturated ketone distilled off (temperature in vapor 71-73°) and collected in a receiver cooled with ice water. To complete the process the reaction mixture was heated for some time at 150° until reaction product ceased to distill over. In all 159.4 g of liquid, $n^{20}D$ 1.4503, distilled over, and from this by redistillation we obtained 140.7 g (64.5α) of 2,4-dimethyl-3-pentadienone (IV); b.p. 72-73° (110 mm); $n^{20}D$ 1.4484; $d^{20}_4$ 0.8710; found MR 33.83; calculated MR 33.60. Found: C 76.44; 76.40; H 9.28; 9.27%. $C_7H_{10}O$. Calculated: C 76.35; H 9.09%. The 2,4-dinitrophenylhydrazone, prepared in the usual way, formed red prisms, m.p. 200.0-200.5°, after recrystallization from a mixture of ethyl acetate and ethanol. Found: C 54.10; 54.00; H 4.85; 4.83; N 20.11; 19.83%. $C_{13}H_{14}O_4N_4$. Calculated: C 53.80; H 4.83; N 19.30%. In the ultraviolet spectrum of this dinitrophenylhydrazone $\lambda_{max}$ = 368 mμ. Hydrogenation of 2,4-dimethyl-3-pentadienone over $PtO_2$ in methanol led to the original 2,4-dimethyl-3-pentanone, isolated as the known 2,4-dinitrophenylhydrazone, m.p. 94.5-95.5°.

<u>1,3,5-Trimethyl-4-piperidone.</u> To 110 g of 2,4-dimethyl-3-pentadienone ($n^{20}$D 1.4484) we mixed 35 ml of methanol and 120 ml of 37% aqueous methylamine (25% excess). By the application of slight cooling the temperature was kept at 38-43°. The mixture was then heated for one hour at 50°, kept for a few minutes in the vacuum of a water pump to remove excess of methylamine, acidified with 115 ml of concentrated hydrochloric acid, and vacuum-evaporated to dryness. The residue was treated with boiling acetone with an addition of methanol. Cooling, filtering, and washing with a mixture of acetone and methanol gave 118 g (66.5%) of crystals of the hydrochloride of 1,3,5-trimethyl-4-piperidone (I), m.p. 219-220°. Recrystallization from a mixture of ethyl acetate and ethanol did not affect the melting point. Found: N 8.25; 8.06%. $C_8H_{16}ONCl$. Calculated: N 7.89%.

The mother liquor was evaporated, and the residue was dissolved in water, made alkaline with 50% NaOH solution, and treated in an extractor with ether. Distillation gave 33.5 g (23.8%) of 1,3,5-trimethyl-4-piperidone, b.p. 64-67° (9 mm) and $n^{20}$D 1.4536; the hydrochloride prepared from it had m.p. 219-220°, undepressed by admixture of the previously prepared sample. The total yield was 90.3%.

Preparation of 1,3,5-Trimethyl-4-phenyl-4-piperidinol Isomers (V). a) A solution of phenyllithium was prepared from 8.4 g of lithium and 93.5 g of bromobenzene in 280 ml of ether, and over a period of one hour at 6-8° 35.5 g of 1,3,5-trimethyl-4-piperidone (m.p. 219-220°) was added in small portions through the condenser. On the next day the reaction mixture was heated at the boil for one hour, diluted with 50 ml of benzene, cooled, and decomposed with 100 ml of water. The ether-benzene layer was separated and part of the solvent was distilled off; the needlelike crystals that precipitated on the next day were filtered off and washed with ether. We obtained 21 g of the α-isomer of 1,3,5-trimethyl-4-phenyl-4-piperidinol (Vα), m.p. 131.5-132°. Recrystallization from ether did not affect the melting point. Found: C 76.66; 76.80; H 9.69; 9.50; N 6.80; 6.74%. $C_{14}H_{21}ON$. Calculated : C 76.70; H 9.59; N 6.40%.

The hydrochloride of the α-isomer was prepared in the usual way and had m.p. 222.0-222.5° after crystallization from a mixture of ethyl acetate and methanol. From the mother liquor, after further evaporation, we isolated a further 13.75 g of α-isomer, m.p. 131.0-131.5°.

The mother liquor remaining after these operations was evaporated and treated with a dioxane solution of hydrogen chloride. The resulting greasy hydrochloride was washed with ether and dissolved in a boiling mixture of ethyl acetate and methanol. From this solution 1.7 g of the hydrochloride of the β-isomer, m.p. 223.0-225.5°, was precipitated, and after several crystallizations from a mixture of ethyl acetate and methanol it had a constant m.p. of 236.5-237°. The base of the β-isomer of 1,3,5-trimethyl-4-phenyl-4-piperidinol (Vβ) isolated from this hydrochloride had a constant m.p. of 121.0-121.5° (from gasoline) and gave marked depression of melting point in admixture with the α-isomer. Found: C 76.82; 76.72; H 9.54; 9.59; N 6.20; 6.28%. $C_{14}H_{21}ON$. Calculated: C 76.70; H 9.59; N 6.40%.

After repetition of the separation operations we obtained, altogether: 36.25 g (87.6% of the mixture) of α-isomer, 1.9 g (4.6% of the mixture) of β-isomer, and 3.2 g (7.8%) of unseparated residue. The total yield of the individual alcohols was 94.4%.

b) To a solution of phenyllithium obtained from 6.0 g of lithium and 45 ml of bromobenzene in 240 ml of ether gradual addition was made, without external cooling, of 42.8 g of 1,3,5-trimethyl-4-piperidone [b.p. 72.5-74° (12.5 mm); $n^{20}$D 1.4540] diluted with an equal volume of ether. At the end of the reaction the mixture was hydrolyzed with 150 ml of water, and the ethereal layer was separated and partially evaporated. There was a precipitate of 32.1 g of α-isomer, m.p. 131.0-131.5° (Fraction I). After further evaporation we obtained 16.7 g (Fraction II) of crystals of m.p. 105-112°. This fraction was converted into the hydrochloride, which partially crystallized out as a mixture of heterogeneous crystals. As a result of mechanical separation we obtained 1.65 g of the hydrochloride of the α-isomer, m.p. 222.5-223.5°, and 2.7 g of the hydrochloride of the γ-isomer, m.p. 241.0-242°. The rest of the hydrochloride was combined with the hydrochloride obtained from the mother liquor after the separation of Fraction II; the whole was then dissolved in a mixture of ethyl acetate and methanol, and a seed crystal of the hydrochloride of the γ-isomer was added. As a result we isolated a further 3.8 g of the hydrochloride of the γ-isomer m.p. 241.0-242.5°. After several crystallizations from a mixture of ethyl acetate and methanol this hydrochloride had a constant melting point of 244.0-245.0°. The base liberated from the γ-isomer, 1,3,5-trimethyl-4-phenyl-4-piperidinol (Vγ), had a constant melting point of 134.5-135.0° (from gasoline) and melted at 107-121° in admixture with the α-isomer. Found: C 76.40; 76.44; H 9.63; 9.61; N 6.33; 6.48%. $C_{14}H_{21}ON$. Calculated: C 76.70; H 9.59; N 6.40%.

After repetition of the separation operations we obtained, altogether: 41.15 g (87% of the mixture) of the α-isomer and 6.35 g (13% of the mixture) of the γ-isomer. The total yield on the mixture separated was 71.6%.

Hydrochloride of the Propionic Ester of the α-Isomer of 1,3,5-Trimethyl-4-phenyl-4-piperidinol. a) A mixture of 2.0 g of the α-isomer (m.p. 131.5-132.0°) with 4 ml of dichloroethane was treated with propionyl chloride. Crystallization occurred quickly and gave 1.8 g of crystals, m.p. 160-197°. The base isolated from the whole reaction mixture (1.95 g) consisted of crystals with a small amount of oil. Retreatment with propionyl chloride led to the formation of 1.85 g of the original base, which crystallized almost completely.

b) A mixture of 15 g of the α-isomer (m.p. 131.5-132.0°), 20 ml of dry pyridine, and 20 ml of propionic anhydride was heated for six hours at 142-143°. Pyridine and acid anhydride were vacuum-distilled off, and the residue was treated with water and sodium carbonate, extracted with ether, and, after removal of ether, vacuum-distilled. We obtained 17.3 g (91.8%) of oil of b.p. 140-143° (0.02 mm), which formed the hydrochloride quantitatively (19.5 g). After several crystallizations from a mixture of ethyl acetate and methanol the hydrochloride of the propionic ester of the α-isomer of 1,3,5-trimethyl-4-phenyl-4-piperidinol had a constant melting point of 181.0-182.0°. Found: C 65.33; 65.17; H 8.35; 8.31; N 4.65; 4.70% $C_{17}H_{26}O_2NCl$. Calculated: C 65.50; H 8.35; N 4.49%.

Hydrochloride of the Propionic Ester of the β-Isomer of 1,3,5-Trimethyl-4-phenyl-4-piperidinol. A solution of 2 g of the β-isomer (m.p. 120.5-121.0°) in 6 ml of dichloroethane was treated with 3 ml of proprionyl chloride without allowing great rise in temperature. When the evolution of heat had stopped, the mixture was heated at 50° until the small amount of precipitate formed had dissolved (5 minutes). The mixture was left for three days, and after the addition of ether, 2.55 g (89.5%) of crystals, m.p. 165.5-167.0°, was precipitated. After several crystallizations from the mixture of ethyl acetate and methanol the hydrochloride of the propionic ester of the β-isomer of 1,3,5-trimethyl-4-phenyl-4-piperidinol had a constant melting point of 171.0-171.5°. Found: C 64.93; 64.95; H 8.40; 8.29; N 4.51; 4.37%. $C_{17}H_{26}O_2NCl$. Calculated: C 65.50; H 8.35; N 4.49%.

Hydrochloride of the Propionic Ester of the γ-Isomer of 1,3,5-Trimethyl-4-phenyl-4-piperidinol. Propionyl chloride (1.5 ml) was added to a mixture of 1.0 g of the γ-isomer (m.p. 134.5-135.0°) and 1.5 ml of dichloroethane. The precipitate formed was dissolved by heating the mixture for 20 minutes at 50°. The mixture was left for three days, and addition of ether gave 1.4 g of hydrochloride, m.p. 158-188°, and from this we obtained 1.2 g of base as a noncrystallizing oil. A second similar treatment with propionyl chloride gave 1.3 g of hydrochloride, m.p. 175.5-176.6°, and a third gave 1.15 g, m.p. 180.0-181.0°. Two crystallizations from a mixture of ethyl acetate and methanol gave 1.0 g of the hydrochloride of the propionic ester of the γ-isomer of 1,3,5-trimethyl-4-phenyl-4-piperidinol with a constant melting point of 183.0-184.0°. Found: C 65.28; 65.37; H 8.28; 8.22; N 4.47; 4.61%. $C_{17}H_{26}O_2NCl$. Calculated: C 65.50; H 8.35; N 4.49%.

## SUMMARY

1. A method was found for the preparation of 2,4-dimethyl-3-pentadienone from 2,4-dimethyl-3-pentanone.

2. 1,3,5-Trimethyl-4-piperidone was synthesized from 2,4-dimethyl-3-pentadienone. Reaction of the trimethylpiperidone with phenyllithium gave the α-, β-, and γ-isomers of 1,3,5-trimethyl-4-phenyl-4-piperidinol. The hydrochlorides of the propionic esters of these were synthesized.

3. The possible configurations of the compounds synthesized were discussed.

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# CATALYTIC ALKYLATION OF TETRALIN

COMMUNICATION 4. DETERMINATION OF THE STRUCTURES OF ALKYLTETRALINS
WITH THE AID OF INFRARED SPECTROSCOPY

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The physical properties of tetralin homologs have as yet received inadequate study. The data in the literature are extremely contradictory. Constants are frequently given without any indication of the position and structure of the side chain.

To determine the structures of alkyltetralins obtained by alkylation we used the method of infrared spectroscopy. The spectrum investigation had two objects: the determination of the position of the alkyl group, and the determination of its structure. The method of determining the position of the alkyl group is described in one of our previous papers [1]. To resolve the second question we synthesized the following 6-alkyltetralins [2] in the pure state; they contained both normal and branched alkyls:
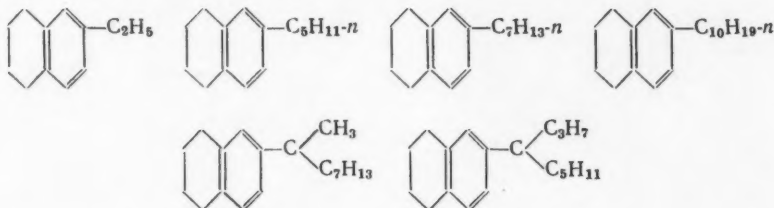


As the infrared spectra of alkyltetralins in the region 650-2000 cm$^{-1}$ (NaCl prism) contain many absorption bands and do not differ greatly for compounds in which the side group is in a given position [1, 3, 4], the use of the usual spectrum characteristics in the determination of the structure of the alkyl group did not appear to be possible. For example, the frequencies 1141 and 1170 cm$^{-1}$, which usually characterize the skeletal vibrations of a tertiary carbon atom [5], fall in a range containing fairly strong bands due to tetralin. A more convenient range for the solution of our problem is found to be that of CH valence vibrations at 2800-3100 cm$^{-1}$ (LiF prism). This range has long attracted the attention of investigators [6, 7, 8], who have in various degrees shown the possibility of using it for analytical purposes, particularly for alkanes. We therefore gave our main attention to CH valence vibrations.

The spectra of the hydrocarbons synthesized were determined with an IKS-12 infrared spectrometer with an LiF prism (2800-3100 cm$^{-1}$). The determination was carried out by the "point" method [9]. The compounds were investigated in CCl$_4$ solution in a cell with constant layer thickness. The concentration was selected for each individual case; it usually did not exceed 0.1%. We compared the intensities ($\epsilon$) of absorption bands with maxima at 2960 ±5 and 2930 ±5 cm$^{-1}$, which belong to the antisymmetrical CH valence vibrations in the CH$_3$ and CH$_2$ groups respectively. These bands are convenient because of their stability and high intensity. Other bands, such as overtones, falling in this region are not significant on the background of the main bands and produce scarcely any distortion of the usual spectrum picture observed for the CH vibrations of an aliphatic chain. By way of example, one of the spectra is shown in Fig. 1, in which $\epsilon$ is the extinction coefficient:

$$\varepsilon = \frac{D \cdot M}{cd}$$

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Intensities of Absorption Bands at 2930 and 2960 cm$^{-1}$ in the Infrared Spectra of 6-Alkyltetralins

| No. | Hydrocarbon | $\varepsilon_1$ | No. of CH$_2$ groups | $\varepsilon_2$ | No. of CH$_3$ groups |
|-----|-------------|------|------|------|------|
| 1 | Tetralin | 195 | 4 | — | — |
| 2 | Ethyltetralin | 245 | 5 | 95 | 1 |
| 3 | Pentyltetralin | 465 | 8 | 110 | 1 |
| 4 | Heptyltetralin | 605 | 10 | 110 | 1 |
| 5 | Decyltetralin | 840 | 13 | 105 | 1 |
| 6 | (1-Propylhexyl)tetralin | 635 | 10 | 210 | 2 |
| 7 | (1-Methyloctyl)tetralin | 640 | 10 | 195 | 2 |
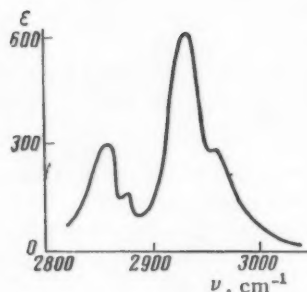


Fig. 1. Spectrum of 6-heptyltetralin in the region of CH valence vibrations.
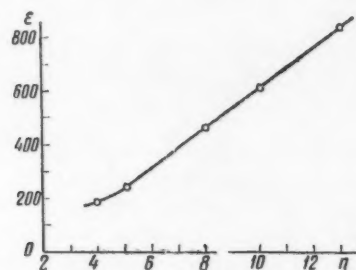


Fig. 2. Relation of the intensity to the absorption band at 2390 cm$^{-1}$ of the number of CH$_2$ groups in 6-alkyltetralins.

In this formula D is optical density, $\underline{c}$ is concentration (g/liter), $\underline{d}$ is the thickness of the absorption layer (cm), and M is molecular weight.

An examination of the results (table and Fig. 2) enables us to state that the effect of the tetralin nucleus on an alkyl group is relatively small and is shown in a certain reduction in the intensity $\varepsilon_1$ of the absorption band due to CH valence vibrations in the CH$_2$ group (2930 cm$^{-1}$). This,and the fact that the position of the absorption bands of the CH$_2$ groups of the hydrogenated ring coincides with that of the absorption of CH$_2$ groups in the side chain, makes it possible to relate intensity with number of CH$_2$ groups in a simple manner. It was found that $\varepsilon_1 = 73n - 120$ (Fig. 2).

For $\varepsilon_2$, the intensity of the band at 2960 cm$^{-1}$ (CH$_3$), lowering is almost absent, which indicates extremely rapid attenuation of the effect of the tetralin ring with increase of distance. In this case the extinction coefficient is expressed by $\varepsilon_2 = 105\underline{n}$.

The laws obtained for the vibration of the extinction coefficients $\varepsilon_1$ and $\varepsilon_2$ with the numbers of CH$_2$ and CH$_3$ groups were checked for the case of tetralins substituted with branched C$_9$ alkyls (No. 6 and 7 in table). Some increase in $\varepsilon_1$ is to be explained by reduction in the effect of the aromatic nucleus on the CH$_2$ group. We consider that similar laws must be observed for alkyltetralins with the alkyl group in other positions in the tetralin nucleus.

## SUMMARY

It was shown to be possible to determine the structures of alkyltetralins by the method of infrared spectroscopy.

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# AMINATION OF BUTYL ALCOHOL OVER IRON CATALYSTS IN PRESENCE
# OF HYDROGEN UNDER PRESSURE

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The catalytic amination of alcohols, which was discovered by Sabatier [1] in 1909, even now continues to attract the attention of a wide circle of investigators [2, 3]; it has been studied in a particularly detailed manner in presence of catalysts based on alumina, and this has led to the establishment of the amination of methanol and some other alcohols on an industrial scale [4, 5]. Over these catalysts the reaction is generally carried out at 350-450° with a large excess of ammonia. Under these conditions at relatively low space velocities with respect to alcohol (about $0.3 \ hr^{-1}$), it has been possible to bring the conversion of butyl alcohol up to 81%. However, the yield of amines on the amount of alcohol converted attained only 70% [6]. Increase in ammonia pressure favors increase in the yield of desired products [7, 8], which in some cases attains 90% on the amount of alcohol that reacted [7].

There is information in patents about the carrying out of the amination of alcohols over metallic hydrogenating catalysts in presence of hydrogen under pressure [9-13]. According to this, amination is carried out at 150-250°, goes with a high conversion of the alcohol per passage (up to 95%), and is characterized by a high yield of amines on the amount of the alcohol converted (up to 97%) [11]. The catalysts used are skeletal Cu—Al, Cu—Si [11], and Ni—Al [9, 13], and also other catalysts based on Group VIII elements [10, 12]. This method for the synthesis of amines has definite advantages over the amination of alcohols in presence of oxide catalysts. In the literature, however, there are no systematic data about the reaction between an alcohol and ammonia over metallic hydrogenation catalysts in presence of hydrogen under pressure. In view of this it appeared to be desirable to carry out a fuller study of this process. As a metallic hydrogenation catalyst we chose an iron catalyst of the type used for syntheses from carbon monoxide and hydrogen. The reaction studied was the amination of butyl alcohol.

## EXPERIMENTAL*

The work was carried out in a high-pressure apparatus, which is shown diagrammatically in Fig. 1. The main components were as follows: A reactor (5) with receiver (6) and provided with an electric heater and thermoregulator. A doser (4) for feeding liquid into the reactor. An autoclave with a bubbler (3), provided with an electric heater. Before the experiment this was filled with liquid ammonia. Charcoal adsorber (7), pressure regulator (2), and gas meter (9). All the components of the apparatus have been described individually previously [14, 15].

During the experiment a mixture of hydrogen and ammonia was fed into the reactor [5] from the autoclave (3) and butyl alcohol was fed in from the doser (4). After passing through the catalyst layer in the reactor, the reaction mixture passed into the receiver (6), in which it was cooled and separated from liquid reaction products and unchanged alcohol. The outgoing gases were choked by the exit valve down to atmospheric pressure and passed to the absorber (7). In the absorber the gaseous products and the liquid amination products entrained by the outgoing gases were trapped. The hydrogen was purified from ammonia in the vessel (8) containing dilute sulfuric acid and passed to the gas meter (9), from which it was rejected into the atmosphere. The required pressure was maintained in the system by means of the pressure regulator (2). The dosage of ammonia was effected by heating the autoclave (3) to the necessary temperature. The amount of hydrogen passing through the apparatus was controlled by the exit valve and recorded by the gas meter (9). Loss of hydrogen was made good from the cylinder (1).

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*Student N. E. Mak took part in the experimental work.

## TABLE 1

Material Balance in the Amination of Butyl Alcohol over an Iron Catalyst in Presence of Hydrogen under Pressure (p = 100 atm; t = 230°; $v_{H_2}$ = 500 hr$^{-1}$; $v_{alcohol}$ = 57 g/liter·hr; ammonia content of gas 45,5%)

| Alcohol taken | Amt. (g) | Substances obtained | Amount | |
|---|---|---|---|---|
| | | | g | % |
| Butyl alcohol | 111,65 | Amines | 77,6 | 69,6 |
| | | Butyl alcohol | 17,2 | 15,4 |
| | | Butyraldehyde | 2,23 | 2,0 |
| | | Butane + butene | 5,75 | 5,2 |
| | | Losses | 8,87 | 7,8 |
| Total | 111,65 | Total | 111,65 | 100,0 |

## TABLE 2

Effect of Various Factors on the Yield and Composition of Amines in the Amination of Butyl Alcohol over an Iron Catalyst in Presence of Hydrogen under Pressure

| Ammonia content of gas (% by vol.) | Space velocity ($H_2$) (hr$^{-1}$) | Reactor temp. (°C) | Pressure (atm) | Rate of feed of alcohol (g/liter·hr) | Alcohol taken (g) | Molar ratio ammonia:alcohol | Condensate obtained (g) | Amines isolated (g) | Yield of amines (% on alcohol taken) | Productivity of catalyst (g/liter·hr) | Composition of amines (moles %) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | primary | secondary | tertiary |
| *Effect of ammonia content of original gas mixture* | | | | | | | | | | | | | |
| 8,5 | 526 | 230 | 100 | 119,0 | 30,15 | 1,36 | 29,82 | 11,20 | 37,0 | 43,6 | 75,0 | 20,8 | 4,2 |
| 25,5 | 490 | 230 | 100 | 110,0 | 30,05 | 5,05 | 28,90 | 12,45 | 41,2 | 45,3 | — | — | — |
| 40,9 | 460 | 230 | 100 | 115,0 | 30,04 | 8,95 | 29,74 | 13,40 | 44,3 | 50,9 | 91,2 | 8,8 | Traces |
| 51,0 | 560 | 230 | 100 | 112,0 | 30,26 | 17,20 | 30,10 | 14,40 | 47,5 | 53,0 | 93,0 | 7,0 | » |
| *Effect of space velocity with respect to hydrogen* | | | | | | | | | | | | | |
| 40,9 | 64 | 230 | 100 | 108 | 25,14 | 1,33 | 24,45 | 8,85 | 35,2 | 38,2 | 66,5 | 30,0 | 3,5 |
| 40,9 | 272 | 230 | 100 | 112 | 29,73 | 5,47 | 29,50 | 12,40 | 42,0 | 46,5 | 89,8 | 10,2 | Traces |
| 40,9 | 460 | 230 | 100 | 115 | 30,04 | 8,95 | 29,74 | 13,40 | 45,3 | 50,2 | 91,2 | 8,8 | » |
| 40,9 | 1150 | 230 | 100 | 121 | 30,27 | 21,4 | 30,10 | 17,50 | 58,0 | 69,5 | 92,4 | 7,6 | » |
| 40,9 | 1800 | 230 | 100 | 125 | 30,29 | 32,4 | 30,61 | 18,10 | 59,8 | 75,0 | 91,8 | 8,2 | » |
| *Effect of temperature* | | | | | | | | | | | | | |
| 40,9 | 1340 | 190 | 100 | 115 | 28,39 | 26,2 | 28,20 | 7,15 | 25,1 | 28,0 | 93,66 | 6,34 | Traces |
| 40,9 | 1150 | 230 | 100 | 121 | 30,27 | 21,4 | 30,10 | 17,50 | 58,0 | 69,5 | 92,4 | 7,6 | » |
| 40,9 | 1230 | 250 | 100 | 117 | 30,77 | 23,8 | 30,15 | 20,0 | 65,0 | 76,0 | 92,2 | 7,8 | » |
| 40,9 | 1240 | 270 | 100 | 127 | 30,94 | 21,9 | 29,42 | 12,40 | 40,0 | 50,7 | 90,45 | 9,55 | » |
| 40,9 | 1250 | 300 | 100 | 113 | 30,66 | 24,9 | 17,06 | 1,35 | 4,4 | 5,0 | 83,4 | 16,6 | » |
| *Effect of pressure* | | | | | | | | | | | | | |
| 40,9 | 1150 | 230 | 100 | 121 | 30,27 | 21,4 | 30,10 | 17,50 | 58,0 | 69,5 | 92,4 | 7,6 | Traces |
| 40,0 | 1180 | 230 | 50 | 119 | 30,33 | 21,9 | 30,00 | 17,95 | 59,4 | 70,6 | 93,2 | 6,8 | » |
| 43,5 | 1160 | 230 | 20 | 122 | 30,22 | 24,3 | 29,85 | 18,2 | 60,2 | 73,5 | 93,9 | 6,1 | » |
| 40,9 | 1230 | 250 | 100 | 117 | 30,77 | 23,8 | 30,15 | 20,0 | 65,0 | 76,0 | 92,2 | 7,8 | » |
| 43,5 | 1190 | 250 | 20 | 124 | 25,65 | 24,4 | 24,35 | 17,5 | 68,0 | 84,2 | 92,8 | 7,2 | » |
| *Effect of space velocity with respect to alcohol* | | | | | | | | | | | | | |
| 43,5 | 1210 | 230 | 20 | 258 | 40,83 | 11,94 | 35,45 | 19,3 | 47,3 | 122 | 91,8 | 8,2 | Traces |
| 43,5 | 1160 | 230 | 20 | 122 | 30,22 | 24,3 | 29,85 | 18,2 | 60,2 | 73,5 | 93,9 | 6,1 | » |
| 43,5 | 1250 | 230 | 20 | 100 | 28,06 | 31,9 | 28,54 | 18,7 | 66,7 | 66,7 | 94,9 | 5,1 | » |
| 43,5 | 1200 | 230 | 20 | 54,5 | 25,29 | 56,1 | 24,14 | 19,2 | 76,0 | 41,5 | 95,7 | 4,3 | » |
| 43,5 | 1180 | 250 | 20 | 180 | 26,39 | 16,7 | 22,30 | 16,3 | 62,0 | 112,0 | — | — | — |
| 43,5 | 1190 | 250 | 20 | 124 | 25,65 | 24,4 | 24,35 | 17,5 | 68,0 | 84,2 | 92,8 | 7,2 | » |
| 43,5 | 1230 | 250 | 20 | 98,5 | 26,81 | 31,8 | 19,32 | 9,75 | 36,2 | 35,6 | — | — | — |
| 43,5 | 1310 | 250 | 20 | 58,2 | 23,83 | 57,3 | 13,63 | 4,77 | 20,0 | 11,7 | — | — | — |

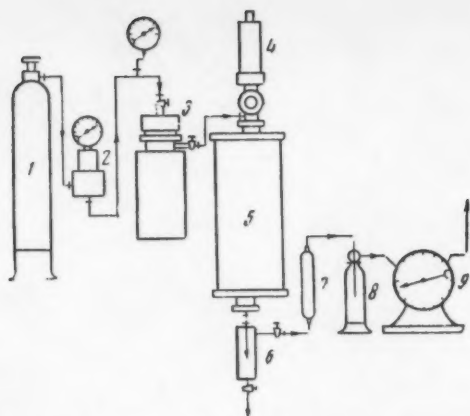*The yield of condensate is given with neglect of liquid desorption products.

Fig. 1. Diagram of laboratory apparatus for the amination of alcohols in presence of hydrogen under pressure.

In the experiments we used doubly distilled butyl alcohol having the following constants: b.p. 116.5° (757 mm); $d^{20}_4$ 0.8120; $n^{20}D$ 1.3989. For butyl alcohol the literature gives: b.p. 117.0° [16]; $d^{20}_4$ 0.8097 [16]; $n^{20}D$ 1.3992 [17]. The liquid reaction products were acidified with dilute (1:1) hydrochloric acid. Unchanged alcohol and neutral products of its reaction were distilled off together with water from amine salts in a Favorskii flask. The solution of amine salts was washed with ether and made alkaline. The amines liberated were extracted with ether and dried with potassium hydroxide. Ether was driven off from the amines by a special procedure that enabled us to obtain comparable results. The amines were analyzed by means of potentiometric titration [18]. When necessary, gaseous products of the synthesis were analyzed in a VTI apparatus, and hydroxyl, aldehyde, and ester values were determined on the neutral part of the catalyzate by standard methods. The possibility of the use of an iron catalyst of the type used for syntheses from carbon monoxide and hydrogen in the amination of alcohols was checked in the course of a preliminary experiment. This experiment was carried out at 100 atm and 230° with a rate of passage of alcohol over the catalyst of 57 g/liter·hr, a space velocity with respect to hydrogen of 500 hr$^{-1}$, and an ammonia content in the original gas mixture of 45.5%. From 111.65 g of butyl alcohol passed over the catalyst we obtained 95.45 g of condensate without liquid desorption products and 2800 ml of gas containing 2.8% of unsaturated and 76.6% of saturated hydrocarbons. The results of the experiment are shown in Table 1.

It will be seen from Table 1 that, assuming that the losses are distributed proportionally to the amounts the corresponding components, the conversion of the alcohol under the given conditions was 83.4%. The reaction of alcohol with ammonia is here characterized by high selectivity: the yield of amines attains 75.6% on the alcohol passed and more than 90.0% on the alcohol that reacts. Calculated on the alcohol passed, the contribution of side reactions does not exceed 8.0%; of this, 2.2% of the alcohol is dehydrogenated and 5.6% is probably dehydrated with subsequent hydrogenation of the butene to butane.

The amines obtained were fractionated through a column of 18-plate efficiency. The bulk (up to 90%) came over at 77.0° (735 mm). The amine isolated in this way had $d^{20}_4$ 0.7400 and $n^{20}D$ 1.4013, and it contained 19.05% of nitrogen. For butylamine the literature [19] gives: b.p. 77.8°; $d^{20}_4$ 0.7401; $n^{20}D$ 1.4010. The theoretical nitrogen content is 19.18%.

In the subsequent investigation we studied the effects on the reaction of butyl alcohol of the ammonia content of the original gas mixture, the space velocity with respect to hydrogen, the temperature, the pressure, and the rate of feed of the alcohol into the reactor. The results are shown in Table 2. From this table it follows that increase in the ammonia content of the gas from 8.5% to 51.0% is accompanied by increase in the yield of amines from 37.0% to 47.5%. There is a simultaneous increase in the proportion of monoalkylamines from 75.0% to 93.0%. Increase in space velocity from 64.0 to 1800 hr$^{-1}$ leads to similar results. The yield of amines increases from 35.2% to 59.8% with simultaneous increase in the proportion of primary amines. A similar effect of amination of 230° is produced by lowering of the space velocity with respect to alcohol. Lowering of the latter from 258 to 54.5 g/liter·hr causes an increase in the yield of amines from 47.3% to 76.0% and a rise in the proportion of primary amines from 91.8% to 95.7%. In all the cases examined the increase in the yield of amines on the amount of alcohol passed and the rise in the proportion of primary amines in the reaction products occurred in conjunction with changes in the amination conditions such as would ensure increase in the molar ratio of ammonia: alcohol. At a given space velocity of alcohol, increase in this ratio was accompanied by increase in the productivity of the catalyst. On the other hand, increase in the ammonia: alcohol ratio due to reduction in the rate of feed of the alcohol into the reactor led to fall in the productivity of the catalyst. Maximum productivity (122 g/liter·hr) was obtained at a space velocity of the alcohol of 258 g/liter·hr. Change in pressure in the range 100-20 atm had no substantial effect on the course of amination at 230-250°.
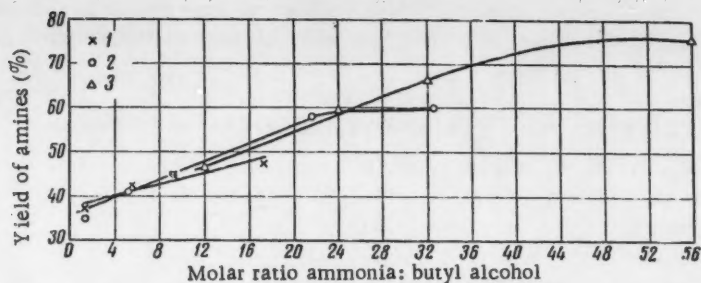
Fig. 2. Relation of yield of amines to the molar ratio ammonia: butyl alcohol.
Results obtained with change in: 1) ammonia content of original gas; 2) space
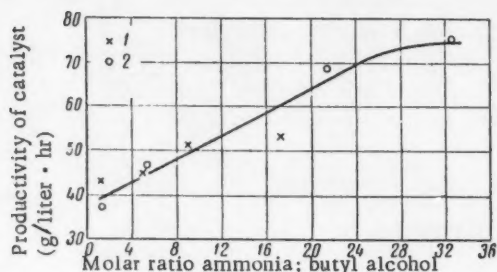velocity of hydrogen; 3) space velocity of butyl alcohol.



Fig. 3. Relation of productivity of catalyst to the
molar ratio ammonia: butyl alcohol. Results ob-
tained with change in: 1) ammonia content of
original gas; 2) space velocity of hydrogen.

On the contrary, temperature has an appreciable
effect on the reaction of the alcohol with ammonia. At
a space velocity of about 120 g/liter·hr, rise in temperature
from 190° to 250° brings about an increase in the yield of
amines from 25.1% to 65%. Further rise to 270°, and
particularly to 300°, brings about a fall in the yield of
amines to 40.0% and 4.4% respectively. This fall in the
yield of amines is probably due to the acceleration of
side processes, which is evidenced by the reduced amount
of condensate obtained in these experiments and the
increased gas formation. Thus, in the experiment at 300°
about 4500 ml of gas containing 0.9% of unsaturated and
66.8% of saturated hydrocarbons was liberated from the
adsorber on desorption.

As will be seen from the results obtained in the
study of the effect of the space velocity of the alcohol on
the amination, the contribution made by side processes
may be great even at 250° at low rates of feed of the alcohol to the catalyst (98.5 and 58.2 g/liter·hr). Rise in
temperature is favorable for the formation of secondary amines. Some of the results given in Table 2 are presented
graphically in Figures 2 and 3. It follows from these results that the molar ratio ammonia: alcohol has a determining
effect on the amination of the alcohol. The curves for the relation of the yield of amines to this ratio, shown in Fig.
2, show that over a fairly wide range of space velocities of the alcohol (100-258 g/liter·hr) and of hydrogen (64.0-
1500 hr$^{-1}$) and with various contents of ammonia in the gas (8.5-51.0%) the proportion of the alcohol converted into
amines is practically determined by the molar ratio ammonia: alcohol, irrespective of the way by which this ratio
is attained. Departures are observed only at high space velocities of hydrogen (above 1500 hr$^{-1}$) and for a low rate
of feed of the alcohol to the catalyst (less than 100 g/liter·hr). It follows from Fig. 3 that at constant temperature
and rate of feed of the alcohol to the catalyst there is a linear relation between the productivity of the catalyst and
the ratio ammonia: alcohol. Departures from this relation occur only as we pass to high space velocities of hydrogen
(about 1500 hr$^{-1}$).

## SUMMARY

1. Iron catalysts of the type used for syntheses from carbon monoxide and hydrogen are suitable for the ami-
nation of alcohols in presence of hydrogen under pressure.

2. For the carrying out of the amination of an alcohol over these catalysts in presence of hydrogen under
pressure, temperatures of 230-250° are favorable. In the ranges studied in space velocity and ammonia content of
the original gas, at a given temperature the molar ratio of ammonia: alcohol has a determining effect on the process.
At a given temperature and rate of feed of alcohol to the catalyst there is a linear relation between the productivity
of the catalyst and this ratio.

3. The highest yield of amines, namely 76.0% on the amount of the alcohol passed, was obtained at 230° and 20 atm with a space velocity of hydrogen of 1200 hr$^{-1}$, an ammonia content of the original gas of 43.5%, and a rate of feed of the alcohol of 54.5 g/liter·hr.

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# SYNTHESIS OF SOME DERIVATIVES OF 1-BENZYL-1H-1,2,3-TRIAZOLE

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In the course of an investigation of polynitrogenous heterocyclic systems we have obtained the following previously undescribed compounds of the v-triazole series: 1-benzyl-1H-1,2,3-triazole-4(or 5)-carboxylic acid (I) and 1-benzyl-1H-1,2,3-triazole-4,5-dimethanol (II).

We carried out the synthesis of the acid (I) in 64.5% yield by the condensation of benzyl azide with propiolic acid under conditions similar to those used for the preparation of 1-benzyl-1H-1,2,3-triazole-4,5-dicarboxylic acid (III) [1].
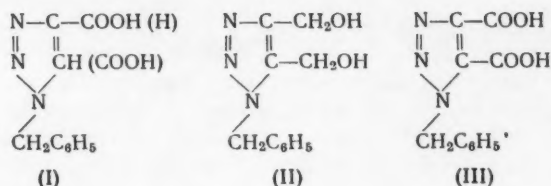


Though we have no experimental data, other than the general course of the condensation, in proof of the position of the carboxy group in the triazole ring, but, on the basis of the considerations of Dimroth [2] regarding the instability of a carboxy group in the position neighboring to an NR group in the pyrazole nucleus and on the analogy between the pyrazole and triazole nuclei, it may be supposed that our product was 1-benzyl-1H-1,2,3-triazole-4-carboxylic acid. Unlike acetylenedicarboxylic and propiolic acids, butyne-1,4-diol condenses with benzyl azide only at higher temperatures with longer reaction times, when it forms the diol (II).

It was of interest to determine the behavior of acids of the v-triazole series in esterification with some nitro alcohols containing various numbers of nitro groups. In the reaction of the acid chlorides of (I) and (III) with 2-nitroethanol in benzene we obtained almost identical yields of 2-nitroethyl 1-benzyl-1H-1,2,3-triazole-4(or 5)-carboxylate (IV) (yield 65%; m.p. 130-131°) and bis-2-nitroethyl 1-benzyl-1H-1,2,3-triazole-4,5-dicarboxylate (V) (yield 56%; m.p. 85-86°).
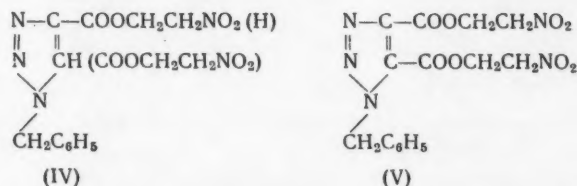


However, in the reaction with 2,2,2-trinitroethanol [3] under analogous conditions, and also in attempts to use other methods of preparing the 2,2,2-trinitroethyl esters of the acids (I) and (III), such as reaction of the acid amide with 2,2,2-trinitroethanol in dilute nitric acid [4], or esterification via mixed anhydrides of the acids [5], the formation of these esters was not detected.

Bis-2-nitroethyl 1-Benzyl-1H-1,2,3-triazole-4,5-dicarboxylate. To 11.2 g of 1-benzyl-1H-1,2,3-triazole-4,5-dicarboxylic acid (0.045 mole) (m.p. 174-175°; obtained in 62% yield [1]) in 50 ml of dry benzene we added 21.0 g of $PCl_5$ (0.1 mole), and the mixture was boiled for nine hours. Benzene and the phosphoryl chloride formed were vacuum-distilled off, a solution of 9 g (0.106 mole) of 2-nitroethanol in 75 ml of dry benzene was added to the residue, and the mixture was boiled further for 3-5 hours. Benzene was distilled off, and the residue was treated with dry ether. The yield of unpurified product was 10.5 g. For purification the crystals were dissolved in acetone, the solution was filtered, and dry ether was added until a turbidity appeared. After one day there separated colorless crystals of bis-2-nitroethyl 1-benzyl-1H-1,2,3-triazole-4,5-dicarboxylate (10.1 g; yield 56%), m.p. 85-86°. The crystals were soluble in dichloroethane and in acetone, but insoluble in ether. Found: C 45.80; 45.85; H 3.89; 3.93; N 17.59; 17.71%. $C_{15}H_{15}O_8N_5$. Calculated: C 45.80; H 3.84; N 17.81%.

1-Benzyl-1H-1,2,3-triazole-4(or 5)-carboxylic acid. One-third of a solution of 14.5 g of benzyl azide in 8 ml of acetone was added with stirring to a solution of 7.6 g of propiolic acid in 18 ml of acetone, and the mixture was then warmed to 50° and gradual addition was made of the remainder of the solution. When the addition was complete, a white precipitate began to form in the mixture. On the next day the precipitate was filtered off and crystallized from water. We obtained 15 g (64.5%) of 1-benzyl-1H-1,2,3-triazole-4(or 5)-carboxylic acid, m.p. 173-174° (from acetone). Found: C 59.13; 59.15; H 4.51; 4.47; N 21.28; 21.05%. $C_{10}H_9O_2N_3$. Calculated: C 59.10; H 4.46; N 20.68%.

2-Nitroethyl 1-Benzyl-1H-1,2,3-triazole-4-carboxylate. To 4.5 g (0.022 mole) of 1-benzyl-1H-1,2,3-triazole 4-carboxylic acid in 40 ml of dry benzene, 5 g of $PCl_5$ was added, and the mixture was heated for 5-6 hours. Benzene and the phosphoryl chloride formed were vacuum-distilled off, and a solution of 2.1 g (0.025 mole) of 2-nitroethanol in 50 ml of dry benzene was added to the residue; the mixture was again heated for eight hours. Crystals that separated out on cooling were filtered off, and crystals separated after the removal of benzene were added to these; they were recrystallized from absolute alcohol. The yield of 2-nitroethyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate was 3.9 g (65%); m.p. 130-131°; colorless gleaming needles. Found: C 52.14; 52.11; H 4.33; 4.41; N 20.48; 20.26%. $C_{12}H_{12}O_4N_4$. Calculated: C 51.97; H 4.36; N 20.26%.

Attempt to Synthesize Bis-2,2,2-trinitroethyl 1-Benzyl-1H-1,2,3-triazole-4,5-dicarboxylate. With the object of preparing this compound several methods were tried:

a) A solution of 2,2,2-trinitroethanol in 20 ml of dry benzene was added to 1-benzyl-1H-1,2,3-triazole-4,5-dicarbonyl chloride prepared as indicated above from 2 g of the acid and 3.6 g of $PCl_5$. The mixture was boiled for five hours, and benzene was then removed in a vacuum. The resulting oil could not be crystallized; it slowly became turbid and decomposed with liberation of 1-benzyl-1H-1,2,3-triazole-4,5-dicarboxylic acid.

b) 1-Benzyl-1H-1,2,3-triazole-4,5-dicarboxylic acid (2 g) was dissolved in 20 ml of concentrated("monohydrate") sulfuric acid, which was first heated to 70-80°. The solution was cooled to room temperature, and addition of seed crystals of the acid did not bring about crystallization. The solution was heated to 35-40° and stirred while 2.6 g of 2,2,2-trinitroethanol was added in small portions; the temperature of the mixture was then raised to 80° and kept at this level for ten minutes. The reaction mixture was cooled and poured into ice water, when only a slight turbidity appeared. The solution was shaken with benzene, and the benzene extract was dried with sodium sulfate. After distillation of the benzene we obtained 2.3 g of an oil, which rapidly crystallized out. The crystals obtained were found to be unchanged trinitroethanol.

c) Hot water (30 ml), concentrated nitric acid (1 ml, sp. gr. 1.4), and a solution of 1.8 g of 2,2,2-trinitroethanol in 10 ml of water were added to 1.2 g of 1-benzyl-1H-1,2,3-triazole-4,5-dicarboxamide (m.p. 199°) [6] prepared by the action of aqueous ammonia on the turbid chloride. The solution was heated with stirring for two hours, and when it was cooled there separated crystals (m.p. 195°), which were found to be unchanged diamide. When water was removed from the mother liquor in a vacuum, an oil was obtained which began to decompose when allowed to stand.

d) Dry ether (30 ml) was added in small portions with stirring to 4 ml of concentrated sulfuric acid ("monohydrate"), and this was followed by 6.4 g of 2,2,2-trinitroethanol and 2 g of acetylenedicarboxylic acid in 15 ml of dry ether. The mixture was heated in a water bath for 25 hours. The resulting clear solution was neutralized with anhydrous sodium carbonate. The ethereal solution was poured off and the precipitate was washed twice with ether;

the ethereal extracts were combined and dried with anhydrous sodium sulfate. After removal of ether in a vacuum, 10 ml of freshly distilled acetone and 3 g of benzyl azide were added to the residue (an oil), and the mixture was boiled with stirring for a further six hours. Acetone was vacuum-distilled off, and the crystals that separated were washed with ether and dried in air; m.p. 166°. After recrystallization from water the melting point was 172°. There was no depression of melting point in admixture with 1-benzyl-1H-1,2,3-triazole-4,5-dicarboxylic acid.

Attempt to synthesize 2,2,2-Trinitroethyl 1-Benzyl-1H-1,2,3-triazole-4(or 5)-carboxylate. To 2 g of 1-benzyl-1H-1,2,3-triazole-4(or 5)-carboxylic acid in 25 ml of dry benzene was added 2.2 g of $PCl_5$, and the mixture was boiled for eight hours. Benzene and the phosphoryl chloride formed were vacuum-distilled off, a solution of 2,2,2-trinitroethanol in 25 ml of dry benzene was added to the residue, and boiling was continued further for 5-6 hours. Benzene was distilled off, and the residue, a mobile yellowish oil, partially crystallized out. The crystals had m.p. 170-172°, undepressed in admixture with 1-benzyl-1H-1,2,3-triazole-4(or 5)-carboxylic acid. Similar experiments carried out at a lower temperature, for longer times (up to seven days), and also with the replacement of benzene by dichloroethane were also unsuccessful.

1-Benzyl-1H-1,2,3-triazole-4,5-dimethanol. Dioxane (100 ml) and benzyl azide (24.5 g; 0.18 mole) were added with stirring to 15.5 g (0.18 mole) of butyne-1,4-diol, and the mixture was boiled for seven hours in a glycerol bath (bath temperature 115-120°). Dioxane was vacuum-distilled off, leaving an oil, which crystallized out on standing. The crystals were separated from oil by pressing out on a porous tile, and washing with ether gave 19.5 g (48%) of unpurified 1-benzyl-1H-1,2,3-triazole-4,5-dimethanol, m.p. 103-104°. Repeated recrystallization from dichloroethane gave crystals of m.p. 108-109°; gleaming white needles, readily soluble in alcohol, dioxane, chloroform, and acetone, poorly soluble in benzene, and insoluble in ether. Found: C 60.32; 60.31; H 5.90; 5.78; N 19.35; 19.36%. $C_{11}H_{13}O_2N_3$. Calculated: C 60.29; H 5.93; N 19.18%.

## SUMMARY

1. The condensations of propiolic acid and of butyne-1,4-diol with benzyl azide were investigated.

2 The condensation of butyne-1,4-diol with benzyl azide requires considerably severer conditions than the condensations of acetylenedicarboxylic and propiolic acids.

3. A study was made of the esterification of mono- and di-carboxylic acids of the v-triazole series with nitro alcohols, and it was shown that with increase in the number of nitro groups in the nitro alcohol the formation of the ester becomes more difficult.

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# REACTION OF $N_2O_4$ WITH ORGANIC COMPOUNDS

COMMUNICATION 6. $\alpha$-NITRO-$\alpha$-NITROSOTOLUENES AND THE MECHANISM OF
THE REACTION BETWEEN $N_2O_4$ AND AROMATIC COMPOUNDS CONTAINING THE
aci-NITRO OR HYDROXYIMINO GROUP IN THE SIDE CHAIN

L. I. Khmel'nitskii, S. S. Novikov, and O. V. Lebedev

It has been noted in previous communications [1, 2] that in the reaction of $N_2O_4$ with benzaldehyde oxamine and $\alpha$-aci-nitrotoluene,by-products of unestablished structure have been observed. It is shown in the present paper that in both cases one of these products was $\alpha$-nitro-$\alpha$-nitrosotoluene, an isomer of benzonitrolic acid:

$$C_6H_5CH{=}NOH \atop C_6H_5CH{=}NOOH \Big\rangle \xrightarrow{N_2O_4} C_6H_5CH{\Big\langle}^{NO}_{NO_2}$$
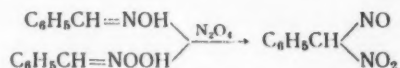
Similarly, from the products of the reaction of $N_2O_4$ with p-chlorobenzaldehyde oxime we isolated p-chloro-$\alpha$-nitro-$\alpha$-nitrosotoluene.

The $\alpha$-nitro-$\alpha$-nitrosotoluenes obtained are compounds of a new type in which a nitro and a nitroso group are present simultaneously on a primary carbon atom. They are colorless powders of characteristic odor, insoluble in ether, sparingly soluble in chloroform and carbon tetrachloride, but somewhat more readily soluble in dichloroethane. When they are dissolved there is a blue coloration corresponding to the transition of the dimeric form of the nitroso compound into the monomeric form. Like the arenecarbonitrolic acids with which they are isomeric, $\alpha$-nitro-$\alpha$-nitrosotoluenes are not very stable: they decompose in the course of one day at room temperature and melt with violent decomposition. The spectroscopic confirmation of the structure of p-chloro-$\alpha$-nitro-$\alpha$-nitrosotoluene will be given in a later paper.

Under the action of aqueous solutions of alkalis, or even under the action of suitable solvents, $\alpha$-nitro-$\alpha$-nitrosotoluenes are isomerized into the corresponding nitrolic acids:

$$ArCH{\Big\langle}^{NO}_{NO_2} \longrightarrow ArC{\Big\langle}^{NOH}_{NO_2}$$

When heated with $N_2O_4$, $\alpha$-nitro-$\alpha$-nitrosotoluenes are converted into $\alpha,\alpha$-dinitrotoluenes:

$$ArCH{\Big\langle}^{NO}_{NO_2} \xrightarrow{N_2O_4} ArCH(NO_2)_2$$
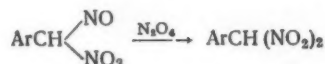
These two reactions permit us to regard $\alpha$-nitro-$\alpha$-nitrosotoluenes as intermediaries in the formation of $\alpha,\alpha$-dinitrotoluenes and arenecarbonitrolic acids from arenecarboxaldehyde oximes and $\alpha$-aci-nitrotoluenes under the action of $N_2O_4$:

$$\left. {ArCH{=}NOH \atop ArCH{=}NOOH} \right\rangle \xrightarrow{N_2O_4} ArCH{\Big\langle}^{NO}_{NO_2} \xrightarrow{N_2O_4} ArCH(NO_2)_2$$
$$\downarrow$$
$$ArC{\Big\langle}^{NOH}_{NO_2}$$
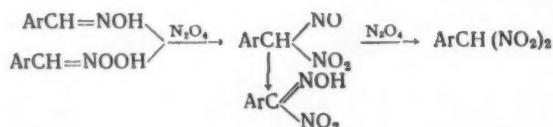
The reactions occurring at a primary carbon atom, which are represented in the horizontal row of the above scheme, fall into line in a natural way with the known reactions leading to the formation of gem-nitronitroso compounds with a secondary carbon atom (pseudonitroles) which occur when $N_2O_4$ reacts with ketoximes [3-9], salts of secondary nitro compounds [10], and $\alpha$-(hydroxyimino) esters [11], and they fall in line also with the oxidation of these nitro nitroso compounds to the corresponding gem-dinitro compounds under the action of various oxidizing agents [4, 8, 9, 11]. Also, like aromatic aldoximes, in some cases ketoximes are converted by $N_2O_4$ into dinitro compounds in a single operation without any arrest at the stage of the formation of nitro nitroso derivatives [12, 13].

Whether the $\alpha,\alpha$-dinitrotoluene or the arenecarbonitrolic acid is preferentially formed is determined by the competition of two directions of reaction of the $\alpha$-nitro-$\alpha$-nitrosotoluene: the isomerization and the oxidation of the nitroso group. Isomerization greatly depends on the nature of the solvent; oxidation is favored by elevated temperature. With a low temperature and a limited amount of $N_2O_4$ oxidation does not occur, but the use of polar solvents (ether, dioxane) favors isomerization, so that under these conditions the nitrolic acid is formed preferentially [14, 15]. In the case of a solvent of low polarity (chloroform, carbon tetrachloride) isomerization is greatly retarded, and the $\alpha$-nitro-$\alpha$-nitrosotoluene can be isolated from the reaction mixture; with excess of $N_2O_4$ this substance is oxidized to the $\alpha,\alpha$-dinitrotoluene. The yield of the latter increases with rise in the reaction temperature; thus, the yield of $\alpha,\alpha$-dinitrotoluene obtained from $\alpha$-aci-nitrotoluene increases from 33.5% to 44.5% on rise in the temperature from 0° to 75°, as shown in the present work. Heating is essential also in the preparation of the $\alpha,\alpha,\alpha$-trinitrotoluene, which is probably also associated with the oxidation of an intermediately formed nitroso compound.

The facts given above together with others that have now accumulated [15-17] enable us to establish mutual relations between the various products of the reaction of $N_2O_4$ with aromatic aldoximes and with $\alpha$-aci-nitrotoluenes and to trace the intermediate stages of the formation of the trinitromethyl group:
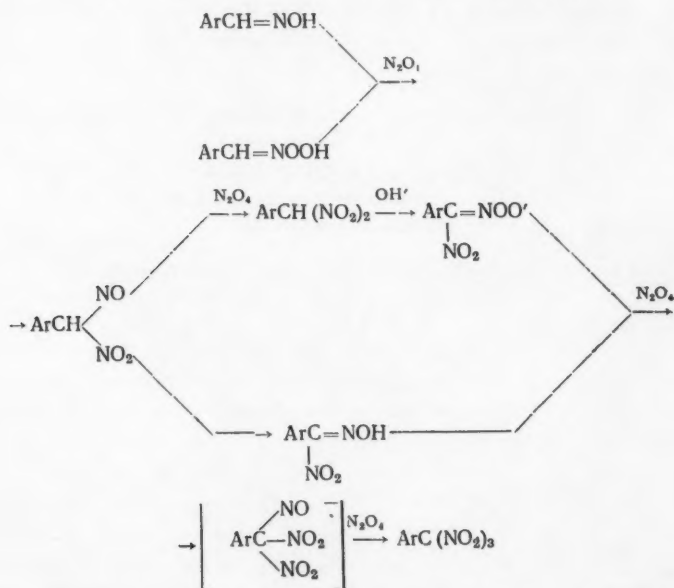


The last intermediate product in this scheme, the $\alpha,\alpha$-dinitro-$\alpha$-nitrosotoluene, has not yet been isolated from the reaction mixture, but its formation is extremely probable on analogy with the formation of the $\alpha$-nitro-$\alpha$-nitrosotoluene from the oxime and from the $\alpha$-aci-nitrotoluene.

In a previous communication [1] some discussion was devoted to the unsatisfactory nature of the scheme proposed by Titov [18] to explain the reaction of $N_2O_4$ with benzaldehyde oxime:

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$$C_6H_5CH=NOH+\cdot NO_2 \rightarrow C_6H_5\overset{.}{C}=NOH+HNO_2$$

$$C_6H_5\overset{.}{C}=NOH+\cdot NO_2 \rightarrow C_6H_5\underset{\underset{NO_2}{|}}{C}=NOH$$

$$C_6H_5\underset{\underset{NO_2}{|}}{C}=NOH+NO_2 \rightarrow C_6H_5CH(NO_2)_2+NO$$

The results obtained in the present work finally exclude Titov's scheme. Benzonitrolic acid is not an intermediary in the formation of $\alpha,\alpha$-dinitrotoluene, and both these compounds are formed from $\alpha$-nitro-$\alpha$-nitrosotoluene, and not from the compounds stated in Titov's scheme. It is as yet difficult to give the actual mechanism of the reaction in detail, but it may already be stated with certainty that, contrary to Titov's scheme, in the conversion of the oxime into the nitrolic acid the $C=N$ bond is affected. This follows not only from the intermediate formation of the $\alpha$-nitro-$\alpha$-nitrosotoluene, but also from the fact that from the pure syn isomer of the oxime a mixture of forms (I) and (II) of the nitrolic acid [16] is formed, i.e., a mixture of syn and anti isomers. The syn-anti isomerism of arenecarbonitrolic acids will be examined in detail in the next communication.

## EXPERIMENTAL

Benzaldehyde and p-chlorobenzaldehyde oximes were prepared by Beckmann's method [19] from the corresponding aldehydes and hydroxylamine. $\alpha$-aci-Nitrotoluene (m.p. 84°) was prepared by the acidification of a solution of the sodium salt of $\alpha$-nitrotoluene with 10% sulfuric acid. The sodium salt of $\alpha$-nitrotoluene was prepared by Titov's method [20].

### Preparation of $\alpha$-Nitro-$\alpha$-nitrosotoluenes

Reaction of $N_2O_4$ with Benzaldehyde Oxime. A solution of 10 g of benzaldehyde oxime in 100 ml of dry carbon tetrachloride was cooled to 0°, and 3.8 g of $N_2O_4$ (0.5 mole per mole of oxime) was added. The reaction mixture turned green, bubbles of gas were liberated, and a white precipitate formed. After 5-10 minutes the precipitate was filtered off, washed with ether, twice with a 50% solution of $N_2O_4$ in ether,* and again with ether (four times), and dried in air at room temperature. The yield of $\alpha$-nitro-$\alpha$-nitrosotoluene was 2 g (14.6%), m.p. 68° (decomp.). Found: C 50.50; 50.50; H 3.69; 3.64%. $C_7H_6N_2O_3$. Calculated: C 50.60; H 3.64%.

Reaction of $N_2O_4$ with p-Chlorobenzaldehyde Oxime. A solution of 2 g of p-chlorobenzaldehyde oxime in 120 ml of dry carbon tetrachloride was cooled to $-10°$, and 0.6 g of $N_2O_4$ (0.5 mole per mole of oxime) was added. The reaction mixture turned green, and a white precipitate formed. After 5-10 minutes the precipitate was treated as in the preceding experiment. The yield of p-chloro-$\alpha$-nitro-$\alpha$-nitrosotoluene was 0.4 g (15.6%), m.p. 71-72° (decomp.). Found: Cl 17.96; 18.02%. $C_7H_5N_2O_3Cl$. Calculated: Cl 17.69%.

Reaction of $N_2O_4$ with $\alpha$-aci-Nitrotoluene. A solution of 0.68 g of $\alpha$-aci-nitrotoluene in 10 ml of dry ether was cooled to 0°, and 0.45 g of $N_2O_4$ (1 mole per mole of $\alpha$-aci-nitrotoluene) was added. The reaction mixture turned green, bubbles of gas were liberated, and a white precipitate formed. After 5-10 minutes the precipitate was filtered off, washed three times with dry ether, and dried in air at room temperature. The yield of $\alpha$-nitro-$\alpha$-nitrosotoluene was 0.1 g (12.2%), m.p. 68° (decomp.). The substance showed no depression of melting point in admixture with $\alpha$-nitro-$\alpha$-nitrosotoluene prepared by the action of $N_2O_4$ on benzaldehyde oxime; the physical and chemical properties of the two substances completely coincided.

### Isomerization of $\alpha$-Nitro-$\alpha$-nitrosotoluenes

Isomerization of $\alpha$-Nitro-$\alpha$-nitrosotoluene. A solution** of 1 g of $\alpha$-nitro-$\alpha$-nitrosotoluene in 10 ml of 5% potassium hydroxide solution cooled to 0° was filtered and neutralized with 50 ml of saturated aqueous oxalic acid, which was also cooled to 0°. The precipitate of benzonitrolic acid was filtered off, washed twice with water, and dissolved in ether. The ether solution was separated from a little potassium oxalate, washed with water, and evaporated in air at room temperature. The yield of benzonitrolic acid was 0.2 g (20%), m.p. 56-57° (decomp.). For benzonitrolic acid the literature [21] gives m.p. 57-58°.

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*To remove the peroxide of benzaldehyde oxime.

**When dissolved in aqueous alkalis, $\alpha$-nitro-$\alpha$-nitrosotoluene and p-chloro-$\alpha$-nitro-$\alpha$-nitrosotoluene give reddish-orange colorations characteristic for alkaline solutions of nitrolic acids.

Isomerization of p-Chloro-$\alpha$-nitro-$\alpha$-nitrosotoluene. A solution of 1 g of p-chloro-$\alpha$-nitro-$\alpha$-nitrosotoluene in 10 ml of 5% potassium hydroxide solution cooled to 0° was filtered and neutralized with 30 ml of 5% hydrochloric acid, which was also cooled to 0°. The precipitate formed was filtered off, washed several times with water, and dried in air at room temperature. The yield of p-chlorobenzonitrolic acid was 0.6 g (60%), m.p. 62-63° (decomp.). The substance showed no depression of melting point in admixture with known p-chlorobenzonitrolic acid obtained by the action of $N_2O_4$ on p-chlorobenzaldehyde oxime; the physical and chemical properties of the two substances completely coincided. For p-chlorobenzonitrolic acid the literature [15] gives m.p. 62-63°.

The isomerization of p-chloro-$\alpha$-nitro-$\alpha$-nitrosotoluene can be effected without the use of alkali. For this it is sufficient to dissolve the substance in acetone. After the evaporation of the solution at room temperature, p-chlorobenzonitrolic acid, m.p. 62-63°, remains as residue.

### Action of $N_2O_4$ on $\alpha$-Nitro-$\alpha$-nitrosotoluenes

To a suspension of 1 g of the $\alpha$-nitro-$\alpha$-nitrosotoluene in 30 ml of dry dichloroethane 4 g of $N_2O_4$ was added, after which the reaction mixture was heated rapidly to 55°. The mixture was washed with water to remove excess of oxides of nitrogen and extracted several times with 10% sodium bicarbonate solution. From the bicarbonate extracts the $\alpha,\alpha$-dinitrotoluene was precipitated with 10% sulfuric acid. The substance was filtered off, washed with water, and dried in air at room temperature. By this procedure $\alpha$-nitro-$\alpha$-nitrosotoluene and p-chloro-$\alpha$-nitro-$\alpha$-nitrosotoluene were converted, respectively, into $\alpha,\alpha$-dinitrotoluene, m.p. 78-79°, and p-chloro-$\alpha,\alpha$-dinitrotoluene, m.p. 55°, in yields of 45.5% and 46.2%.

For $\alpha,\alpha$-dinitrotoluene the literature gives m.p. 79° [22], and for p-chloro-$\alpha,\alpha'$-dinitrotoluene it gives m.p. 55° [14].

### Action of $N_2O_4$ on Benzaldehyde Oxime on Heating

A solution of 2 g of benzaldehyde oxime in 40 ml of dry carbon tetrachloride was heated to 75°, and 3 g of $N_2O_4$ (2 moles per mole of oxime) was added. The reaction mixture foamed up vigorously. The mixture was cooled, washed with water, and extracted with a saturated sodium bicarbonate solution. Acidification of the bicarbonate extracts gave 1.55 g (52%) of $\alpha,\alpha$-dinitrotoluene, m.p. 78-79°.

### SUMMARY

1. $\alpha$-Nitro-$\alpha$-nitrosotoluenes were prepared for the first time, and their properties are described.

2. The chemistry of the conversion of the aldoxime and aci-nitromethyl groups into the dinitro- and trinitromethyl groups under the action of $N_2O_4$ was established.

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# LACTONES AND LACTAMS

## COMMUNICATION 18. REACTION OF N-VINYL LACTAMS WITH HYDROGEN CHLORIDE AND ALCOHOLS

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As shown previously, N-vinyl lactams are active substances and take part both in ionic reactions (hydrolysis [1], dimerization [2]), and in free-radical reactions (polymerization [3], addition of hydrogen sulfide [4]). With the view of extending the ionic reactions of N-vinyl lactams, in the present work we studied the reaction of these compounds with hydrogen chloride and alcohols.

In the action of hydrogen chloride on N-vinyl lactams there is a vigorous reaction with the evolution of much heat. By the interaction of equiomolecular amounts of these compounds extremely unstable adducts are formed. Already after 2-3 hours they are decomposed almost completely into lactam, hydrogen chloride, and resinous residues. Such decomposition is accelerated by heating and the action of atmospheric moisture. The lactams and hydrogen chloride liberated react immediately with formation of crystalline hydrochlorides. Under the action of water the adducts are hydrolyzed with liberation of acetaldehyde and hydrochloric acid. Reaction in a similar way has been observed previously in the hydrolytic decomposition of alkyl 1-chloroethyl ethers [5]:

$$CH_2=CHOR+HCl \rightarrow CH_3CHClOR \xrightarrow{H_2O} CH_3CHO+HCl+ROH.$$

By the action of alcohols on the adducts it was proposed to obtain N-1-alkoxyethyl lactams. However, in this case the adducts decomposed with the liberation of lactam hydrochlorides and resin just as in the case of treatment with atmospheric moisture. Hence, attempts to establish the structures of the products of the reaction of N-vinyl lactams with hydrogen chloride by chemical means were not successful. It was impossible to carry out spectroscopic investigation because of the high fluorescence of the solutions to be analyzed. The experimental data available indicate that hydrogen chloride reacts with N-vinyl lactams by addition; the unstable products then formed appear to consist of a mixture of compounds, which may include the following:

$$CH_2=CHN(CH_2)_nCO + HCl \left\{ \begin{array}{l} CH_3CHClN(CH_2)_nCO \\ CH_2=CHN(CH_2)_nCO \cdot HCl \\ CH_3CHClN(CH_2)_nCO \cdot HCl \end{array} \right.$$

$n = 3{:}5$
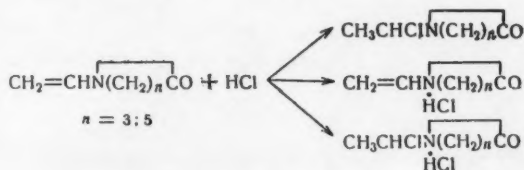
The action of catalytic, not equimolecular amounts, of hydrogen chloride on N-vinyl lactams was studied by Breitenbach and co-workers [6] for the case of 1-vinyl-2-pyrrolidinone. It was shown that small amounts of hydrogen chloride bring about the dimerization of 1-vinyl-2-pyrrolidinone. The following reaction scheme was proposed [6]:

1) $CH_2=CHN(CH_2)_3CO + H^+ \longrightarrow CH_3\overset{+}{C}HN(CH_2)_3CO$

2) $CH_3\overset{+}{C}HN(CH_2)_3CO + CH_2=CHN(CH_2)_3CO \longrightarrow$

$$\longrightarrow CH_3\overset{N(CH_2)_3CO}{C}H \overset{}{----} CH_2 \overset{+}{\underset{N(CH_2)_3CO}{C}}H \longrightarrow$$

$$\longrightarrow CH_3\overset{N(CH_2)_3CO}{C}H \overset{}{----} CH = \overset{N(CH_2)_3CO}{C}H + H^+$$
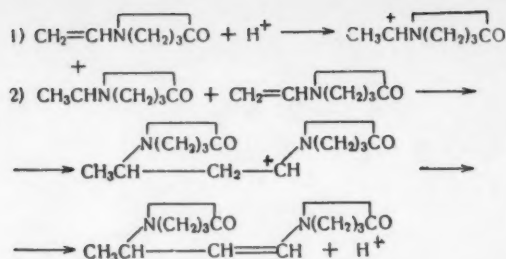
The authors of the present communication have also observed the formation of dimers of 1-vinyl-2-pyrrolidinone and of N-vinylcaprolactam under the action of small amounts of hydrogen chloride. In the course of a study of the dienophile activity of N-vinyl lactams it was found that the dimerization of these monomers in good yield occurs not only on addition of pure hydrogen chloride, but also in a medium of hexachlorocyclopentadiene, in which traces of hydrogen chloride are always present [2]. In this last case, apart from dimers of N-vinyl lactams, no other products were isolated. In this connection it is interesting that alkyl vinyl and aryl vinyl ethers, which are usually readily activated under the influence of hydrogen chloride [7] (in hydrolysis, polymerization, acetal formation), form diene-synthesis adducts with hexachlorocyclopentadiene [2, 8].

This peculiar course of the reaction of N-vinyl lactams and the observed readiness of their activation by hydrogen chloride prompted us to reexamine the reaction of N-vinyl lactams with alcohols catalyzed by hydrogen chloride. Only isolated experiments have previously been carried out on the reaction of N-vinyl lactams with alcohols, and as a result of these N-1-alkoxyethyl lactams were obtained in about 10% yield [9]:

$$CH_2=CHN(CH_2)_nCO + ROH \longrightarrow CH_3\overset{}{\underset{OR}{C}}HN(CH_2)_nCO$$
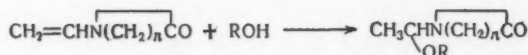
N-1-Alkoxyethyl lactams have been synthesized in better yield by the reaction of 1-chloroethyl ethers with lactams (up to 70% yield of N-1-alkoxyethylcaprolactams [9, 10] and up to 30% yield of 1-(1-alkoxyethyl)pyrrolidinones [11]).

A recent investigation of the ultraviolet spectra of N-vinyl lactams [6, 12, 13] showed that these substances have intense absorption maxima at 234-235 m$\mu$ . This property has been made use of in the present work in the study of the kinetics of the reaction of N-vinyl lactams with alcohols in presence of very small amounts of hydrochloric acid or hydrogen chloride. As control experiments showed, the N-1-alkoxyethyl lactams formed as a result of this reaction have no absorption maximum in the ultraviolet. Hence, by studying the absorption curves of the reaction mixture after definite intervals of time we observed a diminution in the magnitude of the original maximum. By the extent of this diminution we could observe the start and the duration of the reaction leading to the formation of N-1-alkoxyethyl lactams. In all the cases that we investigated the character of the diminution in the intensities of the maxima of N-vinyl lactams in their reaction with alcohols in presence of hydrochloric acid or hydrogen chlorides was the same. By way of example we give one of the graphs obtained (Fig. 1).

Figure 1 shows the diminution in intensity of the ultraviolet absorption maximum of the reaction mixture in the reaction of N-vinylcaprolactam with methanol.
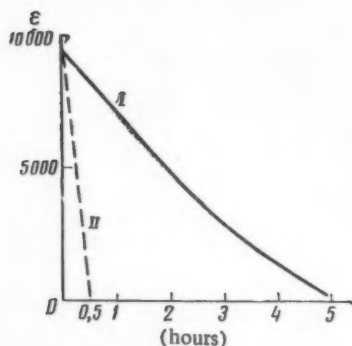


Fig. 1. Measurement of the rate of formation of N-1-methoxyethylcaprolactam: I) amount of catalyst (conc. HCl) 0.0002 g; II) amount of catalyst (conc. HCl) 0.02 g.

The measurements showed that the reaction of 0.05 mole of the N-vinyl lactam with 0.05 mole of the alcohol in presence of 0.02 g of concentrated hydrochloric acid at room temperature is complete in 30 minutes. Here, concentrated hydrochloric acid or dry hydrogen chloride can be used with equal success. Increase in the amount of catalyst, in the duration of the process, and in the degree of heating of the reaction mixture leads to various side processes. As a result of hydrolysis N-vinyl lactams

form lactams and alcohols [1]. The thermal decomposition of N-1-alkoxyethyl lactams gives N-vinyl lactams and alcohols [9-11]. The presence in the reaction product of these side products, which have boiling points close to that of the N-1-alkoxyethyl lactam, considerably increases the difficulty of isolating the latter in the pure state. In these cases it is necessary to employ repeated fractionation, extraction, and other methods with the object of purifying the N-1-alkoxyethyl lactam, and this results in a great reduction in the yield of the desired product. It was found that for the synthesis of N-1-alkoxyethyl lactams in good yield it is necessary to observe the following conditions: Use of catalyst (concentrated hydrochloric acid) in an amount of not more than 0.02 g of 0.05 mole of N-vinyl lactam with neutralization of the catalyst and distillation of the reaction mixture not later than 6-7 hours after the start of reaction. The N-1-alkoxyethyl lactams prepared by the new procedure contain no impurities, and almost pure substances are obtained already after the first distillation. In earlier experiments [11, 12] on the synthesis of these compounds, the reaction conditions were considerably more severe, and a result of which by-products appeared and the yield of N-1-alkoxyethyl lactam was greatly lowered. Hence, the preliminary study of the kinetics of the formation of N-1-alkoxyethyl lactams from N-vinyl lactams and alcohols permitted us to find optimum conditions for the synthesis of these compounds.

## EXPERIMENTAL

Reaction of N-Vinylcaprolactam with Hydrogen Chloride. Hydrogen chloride was passed into a solution of 15 g of N-vinylcaprolactam in 20 g of dry carbon tetrachloride at such a rate that the temperature did not exceed 5°. The passage was continued until absorption of hydrogen chloride ceased. The excess of hydrogen chloride was removed by passage of nitrogen. The reaction mixture was treated with dry ether (50 ml); the viscous mass then precipitated was washed again with ether. From the extracts obtained we isolated 0.5 g of caprolactam hydrochloride, m.p. 135-140° (from dichloroethane), undepressed by admixture of known caprolactam hydrochloride. After drying the viscous mass for one hour at 2 mm we obtained 15.25 g of a substance, which we called the "VC adduct". The VC adduct was soluble in water and ethanol, but insoluble in ether.

A weighed sample of the VC adduct (2.9360 g) was placed in a 200 ml measuring flask and made up with distilled water to the mark; determinations were made of the content of acetaldehyde (bisulfite method) and hydrogen chloride (alkalimetrically and by the Volhard method) in the hydrolyzate (Table 1). When kept, even in a nitrogen atmosphere, the VC adduct was transformed into a black resinous mass.

TABLE 1

Results of the Investigation of the Hydrolyzate of the VC Adduct

| | Hydrogen chloride content (%) | Chlorine content (%) | Acetaldehyde content (%) |
|---|---|---|---|
| Found | 18,61; 18,86 | 18,41; 18,33 | 2,50; 2,10 |
| Calcd. for the formulas | 20,75 | 20,18 | 25,05 |
| CH₃CHClN (CH₂)₅CO | | | |
| CH₂=CHN (CH₂)₅CO | | | |
| HCl | | | |
| Calcd. for the formula | 33,38 | 33,44 | 20,75 |
| CH₃CHClN (CH₂)₅CO HCl | | | |

Reaction of the VC Adduct with Ethanol. An emulsion of 5 g of the VC adduct in 20 ml of dry dichloroethane was added dropwise with stirring and continuous passage of nitrogen into 2.5 g of absolute ethanol. The reaction mixture was neutralized with ammonia, and the ammonium chloride precipitate was extracted with ether. Distillation of the reaction mixture and the ether extract gave 2.29 g of caprolactam (b.p. 118-122° at 4-4.5 mm; m.p. 64-66°) and 3.94 g of resinous residue.

Reaction of 1-Vinyl-2-pyrrolidinone with Hydrogen Chloride. The reaction of 1-vinyl-2-pyrrolidinone with hydrogen chloride was carried out under the same conditions as that of N-vinylcaprolactam. We took 10.0 g of 1-vinyl-2-pyrrolidinone and 20 g of carbon tetrachloride. The maximum reaction temperature was 5°, and the

TABLE 2

Results of the Investigation of the Hydrolyzate of the VP Adduct

| | Hydrogen chloride content (%) | Chlorine content (%) | Acetaldehyde content (%) |
|---|---|---|---|
| Found | 21,48; 21,10 | 21,29; 20,74 | 2,20; 1,48 |
| Calcd. for the formulas | 24,69 | 24,02 | 29,82 |
| $CH_3CHClN(CH_2)_3CO$ | | | |
| $CH_2{=}CHN(CH_2)_3CO$ | | | |
| HCl | | | |
| Calcd. for the formula | 39,62 | 38,59 | 23,92 |
| $CH_3CHClN(CH_2)_3CO$ | | | |
| HCl | | | |

reaction time was 90 minutes. Excess of hydrogen chloride was removed, and the reaction product was precipitated with ether. We isolated 10.5 g of a viscous mass, which we called the "VP adduct". The VP adduct was soluble in water, ethanol, and acetone, and in warm dioxane and benzene; it was insoluble in ether. The analysis of the VP adduct was carried out by the same procedure as that used for the VC adduct. The results of the analysis are presented in Table 2.

Synthesis of N-1-Alkoxyethyl Lactams. To a mixture of 0.05 mole of the N-vinyl lactam and 0.05 mole of the alcohol we added one drop (0.020-0.023 g) of concentrated hydrochloric acid, or hydrogen chloride was passed in through a fine capillary until a rise in temperature was observed. The maximum rise in temperature, 80-130°, was attained in the course of 1-1.5 minutes, and the temperature then fell slowly. After 30 minutes from the start of reaction the reaction mixture was neutralized with potassium carbonate and vacuum-fractionated. The yields, constants, and data of elementary analysis of the N-1-alkoxyethyl lactams obtained are given in Table 3.

## SUMMARY

1. The reaction between N-vinyl lactams and hydrogen chloride is extremely vigorous. When these substances react in equimolecular amounts, unstable products are formed.

2. The kinetics of the addition of alcohols to N-vinyl lactams were studied. The optimum conditions for carrying out this reaction with the object of synthesizing N-1-alkoxyethyl lactams were determined. The yield of these products attained 90%.

TABLE 3
N-1-Alkoxyethyl Lactams

| No. | N-1-Alkoxyethyl lactam | Yield (%) | B.p. in °C (p in mm) | $n_D^{20}$ | $d_4^{20}$ | Found MR | Calcd. MR | Found % C | Found % H | Found % N | Calculated % C | Calculated % H | Calculated % N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1* | 1-(1-Methoxyethyl)pyrrolidinone | 90,3 | 72—72,5 (3,5) | 1,4593 | 1,0434 | 37,53 | 37,92 | 57,94 / 58,03 | 9,13 / 9,21 | 10,50 | 58,72 | 9,15 | 9,88 |
| 2* | 1-(1-Ethoxyethyl)pyrrolidinone | 83,3 | 71—73 (2) | 1,4533 | 1,0125 | 42,00 | 42,54 | 61,24 / 61,11 | 9,31 / 9,38 | 8,89 / 9,13 | 61,12 | 9,61 | 8,91 |
| 3** | 1-(1-Butoxyethyl)pyrrolidinone | 84 | 98—99 (3,5) | 1,4546 | 1,0279 | 46,56 | 47,15 | 63,22 / 63,46 | 10,10 / 9,99 | 8,23 / 8,45 | 63,15 | 10,61 | 8,18 |
| 4* | N-1-Methoxyethylcaprolactam | 90 | 85—86° (2,5) | 1,4708 | | | | | | | | | |
| 5*** | N-1-Ethoxyethylcaprolactam | 82 | 93—95 (2) | 1,4685 | 1,0113 | 42,12 | 42,53 | 61,20 / 61,00 | 9,75 / 9,60 | 9,54 / 9,38 | 61,12 | 9,61 | 8,91 |
| 6*** | N-1-Butoxyethylcaprolactam | 85 | 109—110 (2—2,5) | 1,4660 | | | | | | | | | |
| 7* | 1-(1-Methoxyethyl)piperidone | 85 | 79—80 (3) | 1,4693 | 1,0400 | | | | | | | | |

* These N-1-alkoxyethyl lactams were synthesized for the first time.
** For synthesis see [11].
*** For synthesis see [9].

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# REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

## COMMUNICATION 17. SYNTHESIS OF POLYMERS AND COPOLYMERS OF DIALKYLBIS(3-METHYL-3-BUTEN-1-YNYL)SILANES

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1-Buten-3-yne and its derivatives readily polymerize by the free-radical mechanism [1-4]; the same properties are possessed by compounds containing two 3-buten-1-ynyl groups, e.g., 1,5-octadien-3,5-diyne [5]. There has been no description in the literature of the polymerization and copolymerization of di-3-buten-1-ynyl compounds containing a silicon atom, e.g., substances of the following structure [6]:

$$CH_2=\underset{\underset{CH_3}{|}}{C}-C\equiv C-\underset{\underset{R'}{\diagup}}{\overset{\overset{R}{\diagdown}}{Si}}-C\equiv C-\underset{\underset{CH_3}{|}}{C}=CH_2,$$
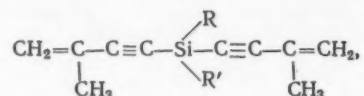
in which R and R' may be H, $CH_3$, $C_2H_5$, or $C_3H_7$.

In the present paper we give the results of our investigations on the polymerization and copolymerization of the following members of this class of compounds: diethylbis(3-methyl-3-buten-1-ynyl)silane, dimethylbis(3-methyl-3-buten-1-ynyl)silane, and methylbis(3-methyl-3-buten-1-ynyl)propylsilane.

The first of these silanes, diethylbis(3-methyl-3-buten-1-ynyl)silane, readily polymerizes in air at room temperature in presence of initiators. The resulting polymers are clear solids and have three-dimensional structures; they undergo no changes when heated to 400°. In the copolymerization of diethylbis(3-methyl-3-buten-1-ynyl)silane with methyl methacrylate there are formed copolymers of various compositions, depending on the concentrations of the monomers in the reaction mixture. The relations of the molar compositions and yields of the copolymers to the concentrations of the monomers are shown in Fig. 1.

As can be seen from Fig. 1, with increase in the concentration of diethylbis(3-methyl-3-buten-1-ynyl)silane in the reaction mixture from 10 to 25 moles per cent the yield of copolymer falls and then changes only slightly. The proportion of silane units in the copolymer increases with rise in the concentration of the silane in the reaction mixture. The copolymers obtained are slightly yellowish solids with good dielectric properties: $\rho_V = 10^{17}$-$10^{18}$ ohm·cm.

Diethylbis(3-methyl-3-buten-1-ynyl)silane was used as a cross-linking agent in the polymerization of methacrylic acid and styrene. The results of the experiments are given in Table 1. For comparison we studied the copolymerization of methyl methacrylate with other members of this class of compounds, namely dimethylbis(3-methyl-3-buten-1-ynyl)silane and methylbis(3-methyl-3-buten-1-ynyl)propylsilane, at the same molar proportions (Table 2).

The highest yields and highest contents of silane monomer units were found in copolymers containing units of diethylbis(3-methyl-3-buten-1-ynyl)silane.

## EXPERIMENTAL

The monomers were freshly distilled and had the following properties: Methyl methacrylate: b.p. 30° (60 mm); $n^{20}D$ 1.4510; $d^{20}_4$ 0.936. Methacrylic acid: b.p. 160°, $n^{20}D$ 1.4310; $d^{20}_4$ 1.015. Diethylbis(3-methyl-3-buten-1-ynyl)
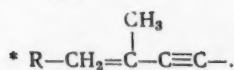
## TABLE 1

Solubilities of Methacrylic Acid and Styrene Polymers Cross-linked with Diethylbis(3-methyl-3-buten-1-ynyl)silane (II)

| Amount of (II) | Yield of polymer (%) | Solubility | |
|---|---|---|---|
| *Methacrylic acid polymers cross-linked with the silane* | | | |
| 0 | 91.5 | Readily soluble in methanol | |
| 0.43 | 94.6 | Readily dissolved in methanol | 26% |
| | | Swells but does not dissolve | 74% |
| 0.86 | 88 | Swells in methanol but does not dissolve | 100% |
| 1.72 | 95 | Swells in methanol | 54% |
| | | Neither swells nor dissolves in methanol | 46% |
| *Styrene polymers cross-linked with the silane* | | | |
| 0.86 | 91 | Swells in benzene | |
| 1.72 | 92 | Swells in benzene | |

## TABLE 2

Copolymerization of Methyl Methacrylate (I) with Dialkylbis(3-methyl-3-buten-1-ynyl)-silanes

| Molar composition of original mixture (%) | | | Yield, % | Molar composition of copolymer (%) | |
|---|---|---|---|---|---|
| formula | (I) | silane | | (I) | silane |
| R*—Si⟨$\begin{smallmatrix}C_2H_5\\ —R\\ C_2H_5\end{smallmatrix}$ | 90 | 10 | 96,0 | 82,21 | 17,29 |
| R—Si—R (with CH$_3$ above and CH$_3$ below) | 90 | 10 | 71,5 | 87,07 | 12,93 |
| R—Si⟨$\begin{smallmatrix}CH_3\\ —R\\ C_3H_7\end{smallmatrix}$ | 90 | 10 | 87 | 86,3 | 13,7 |

$$* \quad R—CH_2=\overset{\underset{\displaystyle CH_3}{|}}{C}—C\equiv C—.$$

silane: b.p. 105° (6 mm); $n^{20}D$ 1.5027; $d^{20}_4$ 0.8594. Dimethylbis(3-methyl-3-buten-1-ynyl)silane: b.p. 75-75.5° (4 mm); $n^{20.7}D$ 1.5000; $d^{20}_4$) 0.8475. Methylbis(3-methyl-3-buten-1-ynyl)propylsilane: b.p. 113° (10 mm); $n^{20}D$ 1.4990; $d^{20}_4$ 0.8555.

The copolymerization reaction was carried out continuously at 60 ± 1° for 100 hours. The monomers were taken in various molar proportions. As initiator we used azobisisobutyronitrile in an amount of 0.2% on the total weight of monomers. Under the same conditions control experiments were carried out in order to study the polymerization of the individual monomers. At the end of the reaction the ampoules were cooled to 0°. The solubilities of the copolymers were then determined. After removal of monomers the copolymers were dried to constant weight. The silicon contents of the copolymers were then determined, and their compositions were calculated.

Copolymerization of Methyl Methacrylate (I) with Diethylbis(3-methyl-3-buten-1-ynyl)silane (II) (Molar Ratio 1: 1). In the course of 100 hours a mixture of 1.58 g (0.0158 mole) of methyl methacrylate and 3.42 g (0.0158 mole) of diethylbis(3-methyl-3-buten-1-ynyl)silane was converted into a not very brittle yellow solid, infusible and

TABLE 3

Copolymerization of Methyl Methacrylate (I) with Diethylbis(3-methyl-3-buten-1-ynyl)silane (II)

| Molar proportions of monomers (%) | | Yield of copoly-mer (%) | Si found (%) | Molar composition of copolymer (%) | |
|---|---|---|---|---|---|
| I | II | | | I | II |
| 100 | — | 97 | — | 100 | — |
| 90 | 10 | 96 | 3,83 4,23 | 82,21 | 17,79 |
| 75 | 52 | 52 | 10,51 10,47 | 33,9 | 66,1 |
| 50 | 50 | 58 | 11,31 11,45 | 23,42 | 76,58 |
| 25 | 75 | 53,5 | 12,12 12,01 | 14,26 | 85,74 |
| 10 | 90 | 54 | 12,47 12,61 | 7,05 | 92,95 |
| — | 100 | 55,6 | 12,6 12,99 | — | 100 |

TABLE 4

| Original molar proportions of monomers (*) | | Original amounts of monomers (g) | | Amounts of monomer units in copolymer | | Amounts of monomer units in copolymer (% by wt.) | |
|---|---|---|---|---|---|---|---|
| I | II | I | II | I | II | I | II |
| 90 | 10 | 4,03 | 0,97 | 4 | 0,89 | 82 | 18 |
| 75 | 25 | 2,91 | 2,09 | 0,5 | 2,08 | 19,4 | 80,6 |
| 50 | 50 | 1,58 | 3,43 | 0,358 | 2,54 | 12,35 | 87,65 |
| 25 | 75 | 0,67 | 4,34 | 0,19 | 2,485 | 7,12 | 92,88 |
| 10 | 90 | 0,244 | 4,76 | 0,092 | 2,62 | 3,39 | 96,61 |
| — | 100 | — | 5 | — | 2,72 | — | 100 |

TABLE 5

Copolymerization of Methyl Methacrylate (I) with Dimethylbis(3-methyl-3-buten-1-ynyl)silane (III) and Methylbis(3-methyl-3-buten-1-ynyl)propylsilane (IV)

| Original molar proportions of monomers (%) | | | Yield of copoly-mer (%) | Si found (%) | Molar composition of copolymer (%) | | | Notes |
|---|---|---|---|---|---|---|---|---|
| I | III | IV | | | I | III | IV | |
| 90 | 10 | — | 71,5 | 3,32 3,44 | 87,07 | 12,93 | — | Hard copolymer |
| 90 | — | 10 | 87 | 2,89 2,81 | 86,3 | — | 13,7 | Very hard copolymer |

insoluble in organic solvents, which gives us reason to regard it as a three-dimensional copolymer. The reaction product was covered with 20 ml of benzene. After a time the benzene solution was poured off, and the slightly swollen residue was again covered with benzene. Washing with benzene was continued until there was no longer a reaction for the double bond. The benzene solution was analyzed for methyl methacrylate content by the hydrolysis method. The amount of diethylbis(3-methyl-3-buten-1-ynyl)silane that had not entered the copolymer was determined by its isolation from the benzene solution. The washed copolymer was dried to constant weight, ground, and analyzed for silicon content.
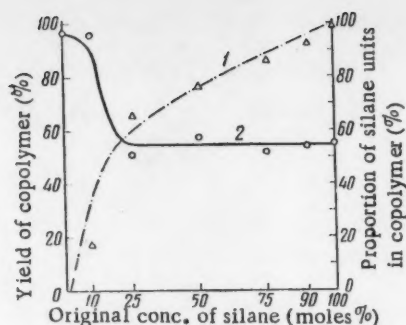
Fig. 1. Relation of molar composition (1) and
yield of copolymer (2) of methyl metha-
crylate and diethylbis(3-methyl-3-buten-1-
ynyl)silane to concentrations of original
monomers.

Under the same conditions the copolymerization of methyl methacrylate with diethylbis(3-methyl-3-buten-1-ynyl)silane was carried out at other molar ratios. The results of the investigations are given in Table 3.

The material balance of the reaction products was drawn up (Table 4).

Below (Table 5) we give results on the copolymerization of methyl methacrylate with dimethylbis(3-methyl-3-buten-1-ynyl)silane and methylbis(3-methyl-3-buten-1-ynyl)propylsilane.

## SUMMARY

1. The copolymerization of methyl methacrylate with dialkylbis(3-methyl-3-buten-1-ynyl)silanes was studied.

2. Copolymers of methyl methacrylate with diethylbis(3-methyl-3-buten-1-ynyl)silane, with dimethylbis(3-methyl-3-buten-1-ynyl)silane, and with methylbis(3-methyl-3-buten-1-ynyl)propylsilane were synthesized; they have good dielectric properties, and they evidently have three-dimensional structures.

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# HOMOGENEOUS DESTRUCTIVE HYDROGENATION OF PROPYL-
# AND ISOPROPYL-PHENOLS IN PRESENCE OF HYDROGEN UNDER PRESSURE

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The present investigation forms the continuation of a series on the homogeneous destructive hydrogenation of phenol [1] and cresols [2]. In these investigations it was shown that the homogeneous hydrogenation of phenols, like that of aromatic hydrocarbons [3, 4], proceeds by a radical-chain mechanism with the participation of hydrogen. In [2] an examination was made of the effect of the position of the alkyl group on the rate of the homogeneous destructive hydrogenation of the three isomeric cresols and on the compositions of the products. The object of the present work was a study of the effect not only of the position, but also of the structure of the alkyl group on the rate and direction of the homogeneous destructive hydrogenation of the isomeric $C_3$-alkyl-substituted phenols. In 1958 Si Tsu-wei and Kalechits [5] reported that at 475° and an initial pressure of 90 atm in presence of an industrial iron catalyst from p-propylphenol there were formed phenol, p-cresol, p-ethylphenol, p-isopropylphenol, benzene, toluene, ethylbenzene, and propylbenzene. The authors stated that they obtained 28.5% of lower phenols.

There are no data in the literature on the homogeneous destructive hydrogenation of $C_3$-alkyl-substituted phenols. The present paper reports results obtained in a study of the homogeneous destructive hydrogenation of o- and p-propylphenols and o- and p-isopropylphenols in presence of hydrogen under pressure.

## EXPERIMENTAL

The original o- and p-propylphenols were synthesized by Clemmensen reduction of the corresponding ketones. The ketones were prepared by the condensation of propionyl chloride with phenol and subsequent rearrangement of the resulting ether in presence of $AlCl_3$ to give a mixture of 2'- and 4'-hydroxypropiophenones [6]. This mixture was readily separated into its components [4'-hydroxypropiophenone, m.p. 147-148°; 2'-hydroxypropiophenone, a liquid of b.p. 122-124° (10 mm)]. After the separation each ketone was reduced separately. The isopropylphenols (o- and p-) were obtained by the rearrangement of phenol isopropyl ether in presence of $AlCl_3$ [7]. The resulting mixture of o- and p-isopropylphenols was separated by vacuum distillation through a fractionating column.

The alkylphenols obtained were vacuum-distilled (20 mm) through a fractionating column of 25-plate efficiency and then had the following properties: o-propylphenol, b.p. 118-118.5° (20 mm); p-propylphenol, b.p. 124-124.5° (20 mm); o-isipropylphenol, b.p. 109-109.5° (20 mm); p-isopropylphenol, m.p. 61°, b.p. 121-121.5°(20 mm). These constants are close to those given in the literature [8].

The experiments were carried out in a 120 ml stainless steel reactor by the procedure described previously [1, 2]. In each experiment the reactor was charged with 40 g of the original alkylphenol. The initial hydrogen pressure was supplied from a cylinder via a multiplier. The reactor was heated to the required temperature in the course of 90 minutes, and the temperature was then kept constant within ±2° for three hours. When the reactor had cooled, the pressure was slowly released; the liquid products collected in a cooled trap. The reactor was then washed out with ether; the ethereal solution was combined with the liquid products and dried with anhydrous sodium sulfate. The reaction products from two parallel experiments were combined and fractionated through the 25 plate column; until 170° was reached, i.e., up to the phenol fraction, the distillation was carried out at atmospheric pressure, but further distillation was in a vacuum (20 mm). The over-all losses in the discharging of the reactor and the fractionation were generally about 5% by weight.

Fractionational Compositions of Liquid Products (without water) in Experiments at 460°, at an Initial Hydrogen Pressure of 200 atm, and for $\tau$ = 3 hours (percent by weight on original alkylphenol)

| Fraction | Expt. 109, 110 with p-propylphenol | Expt. 111, 112 with p-isopropyl-phenol | Expt. 113, 114 with p-propylphenol | Expt. 115, 116 with o-isopropyl-phenol |
|---|---|---|---|---|
| Benzene (up to 95°) | — | 1,4 | 1,4 | 2,0 |
| Toluene (95-123°) | 2,0 | — | 1,4 | — |
| Ethylbenzene (123-147°) | 1,6 | 1,7 | 1,4 | 2,1 |
| Propylbenzene (147-170°) | 4,3 | 7,2 | 5,0 | 6,5 |
| Vacuum fractionation at 20 mm* | | | | |
| Phenol | 9,3 | 10,1 | 26,6 | 29,0 |
| Cresol | 10,6 | 3,3 | 6,5 | 6,3 |
| Ethylphenol | 7,7 | 4,4 | 5,7 | 5,1 |
| Original phenol | 41,4 | 46,8 | 14,1 | 10,7 |
| Residue | 7,1 | 4,4 | 12,1 | 11,9 |
| Total | 84,0 | 79,3 | 74,2 | 73,5 |

*In experiments with p-propyl- and p-isopropyl-phenols: phenol fraction 80-93°, cresol fraction 93-108°, ethylphenol fraction 108-118°; in experiments with o-propyl- and o-isopropyl-phenols: phenol fraction 80-88.5, cresol fraction 88.5-97°, ethyl-phenol fraction 97-105°.
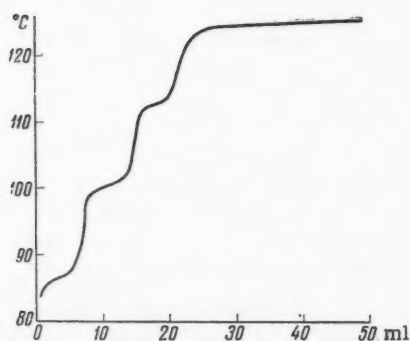


Fig. 1. Fractionation curves of phenol fractions in experiments with p-propyl-phenol (at 20 mm).

All experiments were carried out at 460° with an initial hydrogen pressure of 200 atm (working pressure 370 atm) and for three hours*. The table gives the results of the fractionation of products from experiments with o- and p-propylphenols and with o- and p-isopropylphenols. The fractionation curve (20 mm) of the product of Experiments 109 and 110 is shown in Fig. 1.

An examination of the results enables us to draw the following conclusions: a) Under otherwise equal conditions, the over-all rate of conversion is greater for o-isomers than for p-isomers. b) The over-all rate of conversion of p-propylphenol is somewhat greater than that of p-isopropylphenol. However, for the o-isomers the relation is reversed. Also, as far as can be judged from the composition of the liquid products, the elimination of the whole alkyl group, and also of the hydroxy group, proceeds more vigorously for the isopropylphenols than for the propylphenols. c) At 460° with an initial hydrogen pressure of 200 atm, from o-propyl- and o-isopropyl-phenols 27-29% by weight, i.e., 40 moles per cent, of phenol on the original alkylphenol, may be obtained.

In the homogeneous destructive hydrogenation of the $C_3$-alkyl-substituted phenols, as in the case of the cresols, decomposition of the aromatic ring occurs with formation of carbon monoxide and gaseous hydrocarbons. Analysis of the gaseous reaction products showed that the yield of carbon monoxide was about 1 mole per cent on the original alkylphenol.
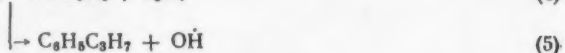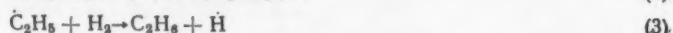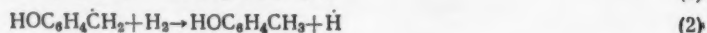
## DISCUSSION OF EXPERIMENTAL RESULTS

In accordance with the views developed in our laboratory, the thermal dissociation of the weakest bond is the first stage in the homogeneous destructive hydrogenation of aromatic hydrocarbons and their derivatives; the free
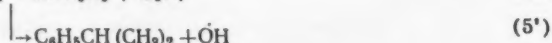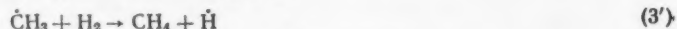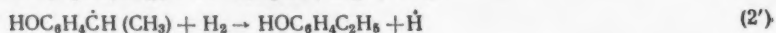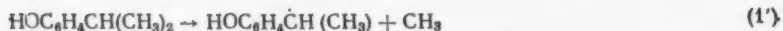
*At 475° and an initial hydrogen pressure of 100 atm there was considerable decomposition of the alkylphenols with formation of a carbonaceous residue.

radicals then formed react with molecular hydrogen with participation of molecules of the original compound [1-4]. This is illustrated in the following schemes[*].

For propylphenol:

$$HOC_6H_4C_3H_7 \rightarrow HOC_6H_4\dot{C}H_2 + \dot{C}_2H_5 \tag{1}$$
$$HOC_6H_4\dot{C}H_2 + H_2 \rightarrow HOC_6H_4CH_3 + \dot{H} \tag{2}$$
$$\dot{C}_2H_5 + H_2 \rightarrow C_2H_6 + \dot{H} \tag{3}$$
$$\dot{H} + HOC_6H_4C_3H_7 \rightarrow HOC_6H_5 + \dot{C}_3H_7 \tag{4}$$
$$\phantom{\dot{H} + HOC_6H_4C_3H_7 } \rightarrow C_6H_5C_3H_7 + \dot{O}H \tag{5}$$

For isopropylphenol:

$$HOC_6H_4CH(CH_3)_2 \rightarrow HOC_6H_4\dot{C}H(CH_3) + CH_3 \tag{1'}$$
$$HOC_6H_4\dot{C}H(CH_3) + H_2 \rightarrow HOC_6H_4C_2H_5 + \dot{H} \tag{2'}$$
$$\dot{C}H_3 + H_2 \rightarrow CH_4 + \dot{H} \tag{3'}$$
$$\dot{H} + HOC_6H_4CH(CH_3)_2 \rightarrow HOC_6H_5 + \dot{C}_3H_7 \tag{4'}$$
$$\phantom{\dot{H} + HOC_6H_4CH(CH_3)_2 } \rightarrow C_6H_5CH(CH_3)_2 + \dot{O}H \tag{5'}$$

It follows from these schemes that the rate of the over-all transformation of alkylphenols under the conditions of homogeneous destructive hydrogenation is determined both by the rate of thermal dissociation of the weakest bond of the alkylphenol in accordance with Eqs. (1) and (1'), and also by the rate of the reaction of atomic hydrogen with a molecule of the original compound in accordance with Eqs. (4), (4'), (5), and (5').

We shall first examine the effect of the position of the alkyl group on the rate of the process studied. In our work [2] on the homogeneous destructive hydrogenation of o-, m-, and p-cresols it was shown that with respect to the rate of over-all transformation these cresols form the series: ortho > para > meta. This result is in accord with the data of Jones and Neuworth [9] on the activation energies for the thermal decomposition of o- and m-cresols (69 and 75 kcal/mole respectively) and also with the data of Szwarc [10] on the activation energies for the bond $CH_3C_6H_4CH_2$ $-H$ in o-, m-, and p-xylenes (74.8, 76.2, and 77.1 kcal/mole respectively). On the basis of this discussion we may suppose with fair certainty that also in the case of $C_3$-alkyl-substituted phenols the thermal decomposition of the o-isomers in accordance with Eqs. (1) and (1') proceeds somewhat more rapidly than that of the p-isomers.

As regards Reactions (4), (4'), (5), and (5'), which include the addition of atomic hydrogen to an aromatic nucleus at a carbon atom carrying a substituent [4], then in the case of alkylphenols as a result of conjugation between the free electron pair of the oxygen atom and the aromatic ring the electron density at the carbon atoms in the o- and p-positions to the hydroxy group will be higher than in the m-position. As a result of this the addition of the free radical should occur more rapidly in the o- and p-positions than in the m-position to the hydroxy group. Our previous results on the rate of the homogeneous destructive hydrogenation of the isomeric cresols and the results of the present work are in agreement with the above considerations. The rate of the over-all transformation is greatest in the case of o-propyl- and o-isopropyl-phenols.

Let us now examine the effect of the structure of the alkyl group on the rate of the homogeneous destructive hydrogenation of alkylphenols. The difference in dissociation energy between the weakest bonds, $C_6H_5CH_2-CH_2CH_3$ in propylbenzene and $C_6H_5CH(CH_3)-CH_3$ in isopropylbenzene, is relatively small; according to the most recent data the dissociation energies are 57.5 and 61 kcal/mole respectively, i.e., somewhat higher for isopropylbenzene. It is to be expected that the same position holds for p-propyl- and p-isopropyl-phenols. However, we may suppose that, when an isopropyl group is present in the o-position to the hydroxy group, some steric strain will be observed which diminishes in the transition state with extension of the bond being broken. In this case the activation energy of Reaction (1') should fall [12]. The above considerations can probably be drawn on in explanation of facts observed in

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[*]Further transformations of the reaction products (e.g., ethylphenol, cresol, etc.) and chain-termination reactions are not considered in these schemes.

the present work: the over-all rate of the transformation of p-propylphenol was somewhat higher than that of p-isopropylphenol, whereas for the corresponding ortho compounds the reverse relation was observed.

In the study of the homogeneous destructive hydrogenation of the isomeric $C_3$-alkyl-substituted phenols it was found also that the elimination of the whole alkyl group, and also of the hydroxy group, from the aromatic ring of p-propylphenol occurs somewhat more slowly than when there is a branching at a $\alpha$-carbon atom of the side chain. A possible explanation of this is provided by a comparison of the induction effects of the propyl and isopropyl groups; it is known that the magnitude of this effect is greater for the isopropyl group, which may be the reason for the high rate constant of Reaction (4'), as compared with that of Reaction (4).

Thus, the effect of the position and structure of the alkyl group in a $C_3$-alkyl-substituted phenol on the rate of the homogeneous destructive hydrogenation of the latter is in general accord with our views on the mechanism of this reaction.

We express our sincere thanks to A. E. Gavrilova for valuable advice on the methods of synthesizing propyl- and isopropyl-phenols.

## SUMMARY

1. The homogeneous destructive hydrogenation of o- and p-propylphenols and o- and p-isopropylphenols was investigated.

2. Under the conditions of homogeneous destructive hydrogenation, a yield of about 40 moles per cent on the original alkyl phenol can be obtained from o-propyl- and o-isopropyl-phenols.

3. An explanation is advanced for the regularities observed that determine the effect of the structure and position of the alkyl group on the rate of the homogeneous destructive hydrogenation of propyl- and isopropyl-phenols and on the composition of the products.

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# SYNTHESIS OF ALKYL-α,α-DIMETHYLCYCLOPROPANEMETHANOLS AND ALKYLCYCLOPROPYL METHYL KETONES

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The synthesis of α-alkylcyclopropanemethanols has been effected by the action of RMgBr (R usually = $C_6H_5$) on alkyl cyclopropyl ketones [1-5] and from cyclopropanecarboxylic esters — also by the Grignard reaction [4, 6, 7, 9]. In the first case the yield of alcohols was 30-50%, and in the second 50-60%. Cases are known of the preparation of cyclopropanemethanols by the reduction of the corresponding ketones with lithium aluminum hydride [8] or with sodium in ethanol [9, 10] and by the oxidation of alkenylcyclopropanes with 2% $KMnO_4$ [11]. For the synthesis of alkyl cyclopropyl ketones the following methods have been most widely used: formation of the three-membered ring from γ-bromo ketones under the action of potassium acetate or of sodium in ethanol [2]; the reaction of alkyl-lithiums with cyclopropanecarboxylic acids [12] and of alkylsodiums with cyclopropanecarboxylic esters [13]. There have recently been synthesized various ketones containing a three-membered ring by the reaction of diazo ketones with unsaturated compounds [14] and of diazoacetic ester with unsaturated ketones in presence or absence of copper [15].

It should be noted that most of the cyclopropanemethanols and cyclopropyl ketones prepared up to now have no alkyl substituents in the three-membered ring. We have prepared little-studied alcohols and ketones having such alkyl substituents. As will be shown below, the presence of these not only has an effect on the physical properties, but sometimes greatly complicates the preparation of such compounds, as they reduce the stability of the three-membered ring.

We carried out the synthesis of such alcohols and ketones from the ethyl alkylcyclopropanecarboxylates that we prepared previously [16]. In our first attempt to prepare an alcohol from ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate and $CH_3MgBr$ we encountered the opening of the three-membered ring, the occurrence of which was established by spectroscopical methods. In our view, this was due to enhanced strain in the three-membered ring in the given compound and under the specific experimental conditions: the use of $CH_3MgBr$ instead of $CH_3MgCl$, and the use of dilute acetic acid instead of pure water from the decomposition of the reaction products. Hence, in further syntheses of cyclopropanemethanols we used $CH_3MgCl$ and treated the reaction products with water only. Cyclopropyl methyl ketones were synthesized by a method used for the synthesis of aliphatic ketones [17, 18]: action of methyllithium on lithium salts of carboxylic acids.

It was found that in the hydrolysis of ethyl alkylcyclopropanecarboxylates with alcoholic lithium hydroxide (heating for 23 hours) the yield of the corresponding lithium salt depends on the structure of the acid. In the case of 2,2,3,3-tetramethylcyclopropanecarboxylic acid the presence of four alkyl substituents creates definite steric hindrance to the hydrolysis, which results in the lowest yield of lithium salt (43%). With two alkyl substituents (2-isopropyl-2-methylcyclopropanecarboxylic acid) the yield of the salt is already 49.5%, and with one substituent (2-butyl-cyclopropanecarboxylic acid) it is at its highest (79.5%).

The effect of the structure of an organic ester on the extent of its hydrolysis was studied by Meyer [19-21], who first demonstrated the part played by steric hindrance on esterification and hydrolysis for the case of o-disubstituted benzoic and phenylacetic acids. The low yields of α,α,2,2,3,3-hexamethylcyclopropanemethanol and methyl 2,2,3,3-tetramethylcyclopropyl ketone are noteworthy and may again be explained by steric hindrance due to the presence of the 2,2,3,3-tetramethylcyclopropyl group in the original compounds.

On comparing the physical properties of ketones and alcohols of given molecular weight we note that with increase in the number of substituents in the three-membered ring: first, the boiling point falls, both of the alcohols and of the ketones; second, the density falls in the case of the alcohols, but rises somewhat in the case of the ketones; third, with increased branching of the substituents the density falls a little in both cases.

Raman spectra were determined* for all the compounds obtained. An examination of them shows that in the case of 2-isopropyl-$\alpha$,$\alpha$,2-trimethylcyclopropanemethanol and 2-isopropyl-2-methylcyclopropyl methyl ketone there is some impurity of a compound containing a double bond. Examination of the spectra of the original esters, which were determined earlier [16], led to the conclusion that opening of the three-membered ring occurred at the stage of the formation of ethyl 2-isopropyl-2-methylcyclopropanecarboxylate.

The reactions of diazoacetic ester with 2,3-dimethyl-2-butene and with 1-hexene gave esters of only alkyl-cyclopropanecarboxylic acids. In the case, however, of 2,3-dimethyl-1-butene the alkylcyclopropanecarboxylic ester was accompanied by an unsaturated aliphatic ester formed by the ring-opening of the alkylcyclopropanecarboxylic exter, which was confirmed by the Raman spectra [16]. Minimum stability of the three-membered ring in ethyl 2-isopropyl-2-methylcyclopropanecarboxylate is in our view associated with the presence of different gem-alkyls (isopropyl and methyl) in the ring.

## EXPERIMENTAL

$\alpha$,$\alpha$,2,2,3,3-Hexamethylcyclopropanemethanol. From 8 g of Mg and $CH_3Cl$ in 200 ml of dry ether we prepared $CH_3MgCl$**, and to this we added a solution of 21 g of ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate in an equal amount of dry ether. The reaction mixture was heated in a water bath for 20 hours, and then decomposed with water. The ether layer was dried with anhydrous $K_2CO_3$. Fractionation gave 10.5 g of the alcohol; yield 54.6%. In an analogous way we prepared 2-butyl-$\alpha$,$\alpha$-dimethylcyclopropanemethanol and 2-isopropyl-$\alpha$,$\alpha$,2-trimethylcyclo-propanemethanol (see table).

Lithium 2,2,3,3-Tetramethylcyclopropanecarboxylate. A mixture of 200 g (1.36 moles) of ethyl 2,2,3,3-tetra-methylcyclopropanecarboxylate with a solution of 31 g (1.3 moles) of lithium hydroxide in 250 ml of ethanol and 150 ml of water was heated in a flask fitted with reflux condenser and stirrer for 23 hours. Water and ethanol were then distilled off from an oil bath, and unchanged original ester was extracted with ether. The salt was dried in a vacuum drying oven for five hours at 60-70° (30 mm). We obtained 74 g (43%) of lithium, 2,2,3,3-tetramethylcyclopropane-carboxylate. In a similar way we prepared the lithium salts of 2-isopropyl-2-methylcyclopropanecarboxylic acid (49.5% yield) and of 2-butylcyclopropanecarboxylic acid (79.5% yield).

Methyl 2,2,3,3-Tetramethylcyclopropyl Ketone. $CH_3Li$ was prepared in a stream of nitrogen from 6 g (0.72 mole) of lithium in 500 ml of dry ether by reaction with $CH_3Cl$. To this was added 50 g (0.36 mole) of lithium 2,2,3,3-tetramethylcyclopropanecarboxylate. The mixture was heated for 20 hours in a water bath and then decom-posed with water. The ether layer was dried with solid KOH. We obtained 20 g (41.7%) of the ketone. The other ketones were prepared similarly (table).

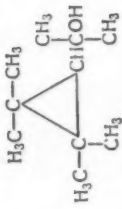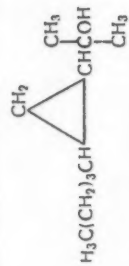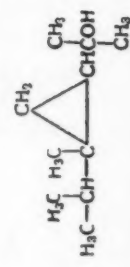$\alpha$,$\alpha$,2,2,3,3-Hexamethylcyclopropanemethanol, $\Delta \nu$ (cm$^{-1}$)

267 (0), 300 (1), 337 (0), 360 (1), 405 (1), 435 (1), 520 (0), 569 (4), 662 (8), 723 (4), 758 (1), 785 (5), 842 (3), 892 (0), 920 (2b), 598 (4b), 1004 (0), 1044 (1b), 1055 (1b), 1114 (3b), 1130 (1b), 1146 (2b), 1170 (0), 1208 (1b), 1335 (1), 1395 (2), 1422 (2), 1446 (4), 1462 (5b), 2870 (4b), 2910 (5b), 2934 (5b), 2975 (6b).
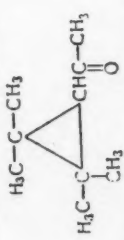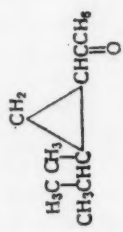
2-Butyl-$\alpha$,$\alpha$-dimethylcyclopropanemethanol, $\Delta \nu$ (cm$^{-1}$)

243 (1), 267 (1b), 290 (1b), 465 (0b), 496 (1b), 556 (1), 590 (2), 613 (1), 632 (1), 655 (1b), 674 (4), 695 (3), 716 (3b), 726 (4b), 780 (0b), 790 (1), 833 (3b), 858 (5b), 863 (4), 880 (1b), 921 (3b), 947 (5b), 958 (2b), 1035 (4b), 1072 (1), 1118 (2b), 1128 (4b), 1222 (1), 1248 (1), 1290 (2), 1305 (1), 1393 (3b), 1450 (10b), 1463 (10b), 1653 (1), 2868 (10), 2900 (8b), 2936 (8), 2965 (10b), 2975 (5), 2990 (10b).

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*The spectra were determined by G. K. Gaivoronskaya of the Optical Group of the Hydrocarbon Chemistry Laboratory.
**We initiated the reaction by the addition of $(H_3C)_3CMgCl$, prepared in a test tube from 1-2 ml of t-butyl chloride and freshly prepared magnesium turnings in 5-10 ml of dry ether.

| Alcohol or ketone | B.p. in °C (p in mm) | $d_4^{20}$ | $n_D^{20}$ | MR | | Yield, (%) | Analytical data | | | | M.p. of semicarbazone (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | found | calcd. | | C (%) | | H, (%) | | |
| | | | | | | | found | calcd. | found | calcd. | |
| α,α,2,2,3,3-Hexamethylcyclopropanemethanol | 69,5 (25) | 0,8472 | 1,4400 | 48,63 | 48,50 | 54,6 | 77,08 76,90 | 76,85 | 12,80 12,75 | 12,90 | |
| 2-Butyl-α,α-dimethylcyclopropanemethanol | 90 (18) | 0,8577 | 1,4420 | 48,19 | 48,50 | 58,0 | 77,16 77,13 | 76,85 | 13,0 12,87 | 12,90 | |
| 2-Isopropyl-α,α,2-trimethylcyclopropanemethanol | 74,5 (19) | 0,8560 | 1,4433 | 48,42 | 48,50 | 83,6 | 76,95 76,58 | 76,85 | 12,30 12,60 | 12,90 | |

| Alcohol or ketone | B.p. in °C, (p in mm) | $d_4^{20}$ | $n_D^{20}$ | MR | | Yield, (%) | Analytical data | | | | M.p. of semi-carbazone (°C) |
| | | | | | | | C, (%) | | H, (%) | | |
| | | | | found | calcd. | | found | calcd. | found | calcd. | |
| Methyl 2,2,3,3-tetramethylcyclopropyl ketone <br> H₃C—C—CH₃ / H₃C—C—CHC—CH₃ / CH₃ ∥O | 59,5 (15) | 0,8655 | 1,4450 | 43,11 | 42,55 | 41,7 | 78,14 77,93 | 77,08 | 11,87 11,98 | 11,50 | 208 (decomp.) |
| 2-Butylcyclopropyl methyl ketone <br> CH₂ / H₃C(CH₂)₃CH—CHCCH₃ ∥O | 78—80 (12) | 0,8639 | 1,4380 | 42,60 | 42,55 | 68,5 | 77,12 77,32 | 77,08 | 11,43 11,52 | 11,50 | 81—82 |
| 2-Isopropyl-2-methylcyclopropyl methyl ketone <br> CH₂ / H₃C CH₃ / CH₃CHC—CHCCH₃ ∥O | 63,5 (17) | 0,8623 | 1,4390 | 42,76 | 42,55 | 63,7 | 76,37 76,18 | 77,03 | 11,41 11,21 | 11,50 | 165—166 |

**2-Isopropyl-α,α,2-trimethylcyclopropanemethanol,** $\Delta \nu$ **(cm$^{-1}$)**

258 (0b), 271 (0b), 339 (0b), 358 (0), 535 (1), 557 (2), 698 (3), 718 (4b), 782 (3b), 800 (1b), 820 (2b), 836 (2), 855 (3b), 891 (3), 922 (4), 948 (2b), 1055 (2), 1083 (2), 1116 (2), 1172 (1), 1202 (5), 1218 (1), 1244 (0), 1298 (3b), 1315 (1b), 1375 (2b), 1409 (3b), 1448 (6), 1452 (5b), 1467 (5b), 2850 (4b), 2968 (4b), 2898 (5), 2914 (5), 2935 (7), 2967 (8), 3002 (10), 3067 (3).

**Methyl 2,2,3,3-tetramethylcyclopropyl ketone,** $\Delta \nu$ **(cm$^{-1}$)**

285 (1b), 362 (0b), 382 (1b), 435 (2b), 484 (1b), 557 (0), 600 (4), 612 (5), 665 (8), 678 (4b), 725 (1), 770 (0b), 825 (1b), 862 (1), 922 (4b), 953 (3b), 967 (3b), 1002 (0), 1032 (1), 1055 (0), 1113 (5b), 1167 (2b), 1191 (2b), 1282 (1b), 1318 (1b), 1338 (3b), 1380 (1), 1397 (2), 1412 (3), 1428 (2), 1463 (3b), 1485 (1), 1690 (4b), 2865 (4b), 2918 (8b), 2955 (5b), 3000 (2b), 3070 (2).

**2-Butylcyclopropyl methyl ketone,** $\Delta \nu$ **(cm$^{-1}$)**

263 (0), 280 (2b), 298 (0), 353 (2b), 385 (3b), 430 (3b), 483 (3), 503 (3), 590 (3), 610 (8), 622 (2), 669 (3), 675 (7), 710 (1), 726 (1), 760 (8b), 772 (8b), 810 (8 ), 825 (8b), 860 (10), 917 (3b), 932 (4b), 953 (2b), 973 (1b), 1002 (1), 1022 (3), 1043 (2), 1070 (2b), 1098 (2b), 1123 (9), 1150 (0), 1177 (2), 1191 (1b), 1240 (5), 1288 (2), 1316 (3), 1363 (1b), 1392 (3b), 1438 (5), 1456 (4b), 1470 (4b), 1635 (1b), 1692 (10b), 2870 (5b), 2915 (7), 2935 (1), 2963 (8), 2996 (1), 3022 (1), 3070 (3).

**2-Isopropyl-2-methylcyclopropyl methyl ketone,** $\Delta \nu$ **(cm$^{-1}$)**

583 (2), 623 (1), 753 (3b), 765 (3b), 785 (2b), 818 (1b), 844 (1b), 863 (2b), 902 (2), 970 (1b), 1040 (1b), 1055 (1b), 1104 (2b), 1118 (3b), 1172 (3b), 1207 (4b), 1303 (1), 1326 (1), 1355 (1), 1398 (2b), 1440 (10b), 1455 (9b), 1695 (4b), 2856 (4b), 2865 (5b), 2896 (3), 2917 (10), 2937 (3 b), 2964 (4), 3003 (8), 3027 (2), 3080 (4).

## SUMMARY

1. Some isomeric alcohols of composition $C_{10}H_{20}O$ and ketones of composition $C_9H_{16}O$, all having a cyclopropane ring containing alkyl groups, were prepared, and their physical properties were compared.

2. Steric hindrance associated with the presence of alkyl substituents in the ring and their number affects the degree of hydrolysis of ethyl alkylcyclopropanecarboxylates and the yields of ketones and alcohols obtained from these esters by organometallic synthesis.

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# SYNTHESIS OF BIFUNCTIONAL DERIVATIVES FROM

## 2,5-DIMETHYLTHIOPHENE

## COMMUNICATION 2. ACTION OF AMINES OF 3,4-BISCHLOROMETHYL-2,5-DIMETHYLTHIOPHENE
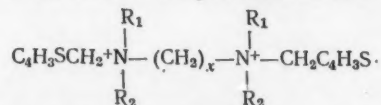
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In a previous communication [1] we have shown that from 2,5-dimethylthiophene by means of simple transformations it is possible to obtain a series of symmetrical quadrisubstituted thiophenes containing two functional groups; derivatives of this type are of interest for investigations on polymeric and also physiologically active compounds. In continuation of work in this direction we decided to study the possibility of synthesis from 2,5-dimethylthiophene of compounds having certain pharmacological properties, in particular the ability to act as hypotensive and curarelike agents.

It is known that such drugs, which block the transmission of nervous impulses in the ganglion or from the nerve to the skeletal muscular system, are used for the treatment of vascular conditions and also in surgical and neurological practice. In the last ten years many compounds (numbered in the thousands) intended for such purposes have been synthesized and to a large extent investigated pharmacologically, but only a few preparations have found practical application. In these connections bisquaternary ammonium salts are of particular interest. The character of the action of the first "methoniums", which are compounds of this type of formula $(CH_3)_3\overset{+}{N}-(CH_2)_n-\overset{+}{N}(CH_3)_3$ and having a symmetrical structure, was considered to be related primarily to the length of the chain between the nitrogen atoms. Recently, however, it was shown [2] that extremely high hypotensive activity is possessed also by many unsymmetrical bisammonium salts in which the connecting chain contained fewer carbon atoms than was previously regarded as essential (5-6). It is interesting that the chain between the nitrogen atoms may form part of a cyclic system [3]. Recent observations have enabled us to reach some important conclusions about the influence of the sizes of the individual fragments of the molecule, steric factors, the distribution of field at the charged nitrogen atoms, etc., on the pharmacological effect. There is great significance in the fact that for unsymmetrical salts there is no direct relation between ganglion-blocking action and hypotensive effect. Other observations also are of significance, for example the fact that ganglion-blocking properties are not always associated with molecules of the onium type since they are found also in some aliphatic-aromatic bistertiary amines [3-6]. In some cases tertiary amines have been found to be more effective than the corresponding bisammonium salts [7]. Hence, the fields of search and the criteria for new drugs of this kind are now considerably more extensive than they were previously.

Among thiophene derivatives, a series of bis-2-thenylammonium salts of formula

$$C_4H_3SCH_2\overset{+}{N}\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{}}-(CH_2)_x-\overset{+}{N}\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{}}-CH_2C_4H_3S \cdot$$

has been tried as ganglion-blocking and curarelike agents. Their activities were found to be about the same as the corresponding bis(benzyldimethylammonium) derivatives. Such a parallelism in power or character of action may not have appeared in a comparison with 3-substituted thiophenes, which show some peculiarities in action, as compared with 2-substituted thiophenes [9].

It was therefore of interest to prepare and study the pharmacological properties of a series of compounds containing the 3-thenyl group in some form or other. In this connection our attention was drawn to the investigations of Rice and others [10] on the chemistry and pharmacology of compounds containing the isoindoline ring in various states of reduction (I). The alkohalides of some of these, while of low toxicity, show strong hypotensive properties.

2,5-Dimethylthiophene might serve as a basis for the building up of similar systems if the stereochemical conditions are the same as in the case of benzene, i.e., if there is a complete analogy between 3,4-bischloromethyl-2,5-dimethylthiophene* (II) and bisbromomethylbenzene (III) in behavior toward amines. The latter, as shown by various investigators [11-14], forms dihydroisoindoles with amines. However, this is only one of the possible courses of the reaction of (III) with amines. In some cases the main reaction is the formation of a noncyclized diamine [15] containing the following grouping
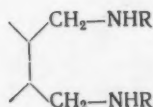


and in other cases it is cyclization with formation of a ten-membered ring [16] or polycondensation with formation of polymeric products.

Ried and Grabosch [14] consider that in the reactions of primary amines with bishalomethyl compounds the degree of symmetry of the latter process is determined rather by stereochemical factors and the associated degree of stability of the compound formed. Such a point of view finds confirmation both in the investigations of the German workers referred to and in our results (see below).

We studied the reaction of BCMDMT (II) with a series of primary (ethyl-, isopropyl-, heptyl-, and t-butyl-amines) and secondary (diethylamine, piperidine, morpholine, and N-methylaniline) amines. Dry benzene was used as reaction medium; except in the experiment with isopropylamine, the ratio of (II) and amine was 1:4. As we passed from one amine to another we endeavored to keep to a constant procedure in the treatment of the mixture obtained, but it was sometimes necessary to depart from this because of change in the distribution of the compounds formed between the aqueous and nonaqueous phases or in the general picture of the experiment. We must point out also that in repeat experiments with a given amine we did not always succeed in attaining identical results. (Results on the reactions of (II) with amines are given in Table 1).

For these reasons at the moment we can speak only of the compounds isolated. This, of course, does not cover the whole question of the nature of the products of the reaction of (II) with amines of different types. Nevertheless, it is already possible to note a characteristic feature of the transformations studied: in all cases the products are symmetrical diamines of structure (IV), (V), and (VII) accompanied by "dimers" of structure (IXa) or (IXb)**. We did not detect compounds analogous to dihydroisoindoline. As in some cases, namely, in the reactions of (II) with heptylamine, t-butylamine, morpholine, and piperidine, the yields of diamines exceeded 50%, it is clear that the process goes predominately in the direction of the formation of the bases (IV) or (V) and (VII). The proportion appearing as diamines (IV) may really be increased on account of the formation of dithienodiazecines (IX), since the former form fragments of the latter.
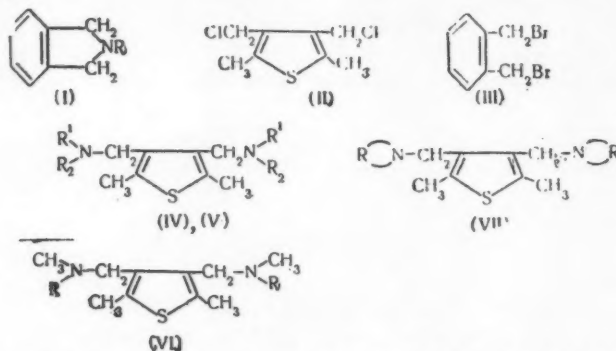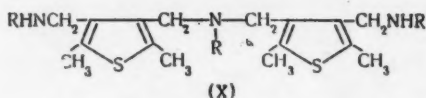
464

(IX)a            (IX)b
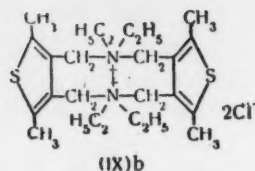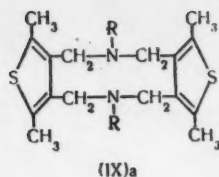
In experiments on the reaction of (II) with isopropylamine, ethylamine, and aniline, in addition to the corresponding diamines (IV), we succeeded in isolating amines of structure (X) (R = $C_2H_5$, i-$C_3H_7$, or $C_6H_5$), which are the structural units of polymers that can be formed in these cases.



(X)

Hence, in its behavior toward aliphatic and aromatic amines BCMDMT (II) differs from o-bisbromomethylbenzene, which forms condensed isoindoline systems, and approaches 1,2-bisbromomethyl-3,4,5,6-tetrachlorobenzene, which gives mainly the corresponding dibenzodiazecine with methylamine [16]. The cause of this difference between BCMDMT and o-bisbromomethylbenzene must be sought in the geometry of these molecules. The valence angle at the 3- and 4-carbon atoms of the thiophene ring (124°5') [17] exceeds that at the carbons of a benzene ring (120°).

For this reason the formation of a condensed five-membered ring is associated with a greater change in the valence angle in the first case than in the second. Roughly the same sort of considerations was advanced by Motoyama and Imoto [18] to explain the possibility of the formation of a six-membered ring with the participation of the amino groups of 3,4-thiophenediamine and the difficulty of obtaining compounds with a five-membered ring from it.

By the action of methylating agents (methyl benzenesulfonate or a mixture of formaldehyde and formic acid) on the diamines (IV) we obtained the bistertiary amines (VI) (Table 2), and only in one case − an attempt to methylate 2,5-dimethyl-N,N'-diphenyl-3,4-thiophenebismethylamine (IV; R = $C_6H_5$) − were we unsuccessful in achieving our object.

When heated in a water bath with methyl iodide in methanol, the diamines (V) gave the corresponding symmetrical bisquaternary salts with two methyl groups on each nitrogen atom. It should be noted that in the case of N,N',2,5-tetramethyl-N,N'-di-t-butyl-3,4-thiophenebismethylamine only a monomethiodide could be isolated under the given conditions.

Some of the methiodides described here were tested pharmacologically and found to have ganglion-blocking and curarelike properties. This question will be discussed in greater detail in à future paper.

### EXPERIMENTAL*

For the reaction of (II) with amines dry benzene was used as solvent: 50-70 ml per 0.1 mole of (II) for amines of serial number (Table 1) 2, 3, 4, 14, 15, 16, and 17, 120 ml for No. 18, and 200 ml for No. 1. The mixing of the reactants was carried out under ice cooling (1, 2, and 4) or at room temperature (3, 5, 14, 15, and 16), after which the mixture was kept at room temperature from 1 to 20 hours, except in the reaction with ethylamine (see below), and then heated in a water bath for 6-8 hours. Data on the products of the reaction of (II) with each of the amines are distributed in accordance with their nature into Sections A, B, C, D, and E (Table 1). For example, the results of the experiment on the reactions of (II) with ethylamine (see below) are given in Sections A, B, and C, and those of the

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*M. A. Vinogradova, a student of the Chemistry Department of the Moscow State University, participated in this work.

# TABLE 1

Products of the Reaction of 3,4-Bischloromethyl-2,5-dimethylthiophene with Amines

A

RHNCH₂—CH₂—NHR (thiophene ring: H₃C, CH₃, S)

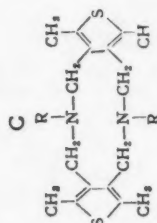$RHNCH_2$—$CH_2$—$NHR$ (2,5-dimethylthiophene)

**(IV) N,N'-Dialkyl-2,5-dimethyl-3,4-thiophenebismethylamine**

| No. | Amine taken in reaction | Molar ratio amine: BCMDMT | R | Formula of product | Yield (%) | M.p., b.p. (°C) (p in mm) | Found (%) | Calculated (%) | Derivatives formula | Derivatives M.p. (°C) | Derivatives found (%) | Derivatives calc. (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Ethylamine | 0,75/0,17 | —$C_2H_5$ | $C_{12}N_{22}N_2S$ | 12—25 | 107—115(2) M.p. 39 from hexane | C 63,55; H 9,86; S 13,97; M 236 | C 63,66; H 9,80; S 14,16; M 226 | Dipicrate $C_{24}H_{28}N_8O_{14}S$ | 156—157 | N 16;09 | N 16,37 |
| 2 | Isopropylamine | 0,38/0,15 | $i$-$C_3H_7$ | $C_{14}H_{26}N_2S$ | 28 | 130—132(6) | C 66,01; H 10,36; S 12,89; N 11,43; M 248 | C 66,09; H 10,30; S 12,60; N 11,02; M 254 | Dipicrate $C_{26}H_{32}N_8O_{14}S$ Dihydrochloride $C_{14}H_{28}Cl_2N_2S$ | 176—177 283 | N 15,34 C 51,01 H 8,60 N 8,26 | N 15,72 C 51,52 H 8,64 N 8,58 |
| 3 | Heptylamine | 0,24/0,06 | —$C_7H_{15}$ | $C_{22}H_{42}N_2S$ | 51 | 200—205(2) | C 71,90; H 11,51; S 8,89; N 7,99 | C 72,07; H 11,55; S 8,75; N 7,65 | Dipicrate $C_{34}H_{48}N_8O_{14}S$ Dihydrochloride $C_{22}H_{44}Cl_2N_2S$ | 160—167 240—241 | N 13,31 M 819 C 60,21 H 10,00 | N 13,59 M 824 C 60,11 H 10,10 |
| 4 | t-Butylamine | 0,41/0,1 | —$C_4H_9$ | $C_{16}H_{30}N_2S$ | 61 | 163—172(7) M.p. 71,5—72,5 | C 68,38; H 10,78; S 11,18; N 9,68; M 272 | C 68,02; H 10,70; S 11,35; N 9,92; M 282 | Dipicrate $C_{28}H_{36}N_8O_{14}S·H_2O$ Dihydrochloride | 204—205 | N 14,45 | N 14,78 |
| 5 | Aniline | 0,37/0,09 | —$C_6H_5$ | $C_{20}H_{22}N_2S$ | 46 | from gasoline M.p. 75—76 from alcohol | C 74,44; H 6,88; S 9,92; N 8,67 | C 74,50; H 6,88; S 9,94; N 8,69 | $C_{16}H_{32}Cl_4N_2S$ MonoPicrate $C_{26}H_{25}N_5O_7S$ | 145 | N 12,26 M 533 | N 12,70 M 551 |

B

$RHN$—$CH_1$— $CH_2$— N—$CH_2$ ... $CH_2NHR$ ($H_3C$—, S, R $H_3C$, S, $CH_3$)

**(X) 4,4'-[[Alkyl(or aryl)imino]dimethylene]bis[N-alkyl(or aryl)2,5-dimethyl-3-thiophenemethyl-amine**

| No. | Amine taken in reaction | Molar ratio amine: BCMDMT | R | Formula of product | Yield (%) | M.p., b.p. (°C) (p in mm) | Found (%) | Calculated (%) | Derivatives formula | Derivatives M.p. (°C) | Derivatives found (%) | Derivatives calc. (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | Ethylamine | See 1 | —$C_2H_5$ | $C_{22}H_{37}N_3S_2$ | 27 | 195—197(2) | C 65,03; H 8,99; S 15,78; N 9,95; M 399 | C 64,81; H 9,15; S 15,73; N 10,31; M 408 | Tripicrate $C_{40}H_{46}N_{12}O_{21}S_2$ | 186—187 | C 44,73 H 4,52 | C 43,87 H 4,23 |

(IXa) 5,11-Dialkyl-4,5,6,10,11,12-hexahydro-1,3,7,9-tetramethyldithieno[3,4-c:3',4'-h] [1,6]diazecine

| № | Amine | See | R | Formula | Yield % | M.p. (prep.) | Found | Calc. | Derivative | M.p. | Found | Calc. |
|---|-------|-----|---|---------|---------|--------------|-------|-------|-----------|------|-------|-------|
| 7 | Isopropyl-amine | See 2 | $i\text{-}C_3H_7$ | $C_{25}H_{41}N_3S_2$ | 3,8 | 195—200(2) | C 66,66; H 9,36; S 14,34; N 9,23 | C 67,06; H 9,23; N 9,39; S 14,32 | Tripicrate $C_{43}H_{50}N_{12}O_{21}S_2$ | 185—186 | C 45,41; H 4,72; S 5,62; M 1123 | C 45,39; H 4,44; S 5,65; M 1135 |
| 8 | Aniline | See 5 | $-C_6H_5$ | $C_{34}H_{37}N_3S_2$ | 17 | from mixture of alcohol and benzene | C 73,71; H 6,75; S 11,60; N 7,62 | C 74,00; H 6,76; S 11,67; N 7,62 | — | — | — | — |
| 9 | Ethylamine | See 1 | $-C_2H_5$ | $C_{20}H_{30}N_2S_2$ | 25—39 | M. p. 88—88,5 from alcohol | C 65,86; H 8,34; S 17,31; N 7,62; M 319 | C 66,29; H 8,28; S 17,67; N 7,73; M 362,6 | Monopicrate $C_{26}H_{33}N_5O_7S_2$ | 250 | N 11,53 | N 11,84 |
| 10 | Isopropyl-amine | See 2 | $i\text{-}C_3H_7$ | $C_{22}H_{34}N_2S_2$ | 11 | M.p. 152—153 from alcohol | C 67,15; H 8,82; S 16,68; N 7,37 | C 67,64; H 8,77; N 7,17; S 16,41 | Monopicrate $C_{28}H_{37}N_5O_7S_2$ | 186 | N 11,59; M 626 | N 11,30; M 619,7 |
| 11 | t-Butyl-amine | See 4 | $-C_4H_9$ | $C_{24}H_{38}N_2S_2{}^*$ |  | M.p. 209—210 from alcohol + acetone | C 68,81; H 8,91; S 15,18; N 6,85; M 406 | C 68,90; H 9,09; S 15,30; N 6,70; M 418,7 | Dipicrate $C_{36}H_{44}N_8O_{14}S_2$ | 195—197 | N 12,36; M 870 | N 12,78; M 876,9 |

| No. | Amine taken in reaction | Molar ratio amine : BCMDMT | R | Formula of product | Yield (%) | M.p., b.p. (°C) (p in mm) | Found (%) | Calculated (%) | Derivatives formula | M.p. (°C) | found (%) | calcd. (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | Diethylamine | 0,4/0,1 | —$C_2H_5$ | $C_{24}H_{40}Cl_2N_2S_2$ | 45 | M.p. 202—204 from alcohol +ether | C 58,54; H 8,12 | C 58,65; H 8,14 | Dipicrate $C_{36}H_{46}N_8O_{14}S_2$ | 157—158 | N 12,70 $M$ 865 | N 12,75 $M$ 879 |
| 13 | Piperidine | 0,4/0,1 | CH₂–CH₂ / CH₂–CH₂ | $C_{26}H_{40}Cl_2N_2S_2$ | 14 | T. пл. 242 from acetone | C 60,22; H 8,20 N 5,22 | C 60,54; H 7,82 N 5,42 | Dipicrate $C_{38}H_{46}N_8O_{14}S_2$ | 246—249 | C 51,10 H 5,02 S 6,95 $M$ 890 | C 50,54 H 5,13 S 7,10 $M$ 903 |
| 14 | Diethylamine | Cm12 | $R_1=R_2=C_2H_5$ | $C_{16}H_{30}N_2S$ | 37 | M.p. 55,5—56,5° from alcohol | C 67,92; H 10,84 S 11,19; $M$ 277 | C 68,03; H 10,71 S 11,35; $M$ 282 | Dipicrate $C_{28}H_{32}N_8O_{14}S$ Dihydrochloride $C_{16}H_{32}Cl_2N_2S$ Dimethiodide ** $C_{18}H_{38}...{}_2N_2S \cdot H_2O$ | 189—191 254 160—165 | N 15,20 C 53,60 H 8,90 C 36,61 H 6,61 N 4,60 43,47 | N 15,13 C 54,08 H 9,07 C 36,99 H 6,55 S 7,10 N 4,79 43,44 |

D

5,5,11,11-Tetraethyl-4,5,6,10,11,12-hexahydro-1,3,7,9-tetramethyl-dithieno[3,4-c:3',4'-h][1,6]diazecinium dichloride
and
4,5,6,10,11,12-hexahydro-1,3,7,9-tetramethyl-5,11-dispentamethylene-dithieno[3,4-c:3',4'-h][1,6]diazecinium dichloride

(IXb)

E

(V)
N,N,N',N'-Tetraalkyl-2,5-dimethyl-3,4-thiophenebismethylamine

and

(VII)
2,5-Dimethyl-3,4-dismorpholino (or piperidino)-methylthiophene

| No | Amine | Structure | b.p. °C/mm | Empirical formula | Yield, % | M.p. | Found | Calc. | Derivative | M.p. | Found | Calc. |
|----|-------|-----------|-----------|-------------------|----------|------|-------|--------|-----------|------|-------|--------|
| 15 | Piperidine | CH$_2$–CH$_2$ / CH$_2$–CH$_2$ with CH$_2$ | Cм. 13 | $C_{18}H_{30}N_2S$ | 71 | M.p. 86,5—87 from alcohol | C 70,56; H 9,76; S 10,58; N 9,08 | C 70,55; H 9,86; S 10,45; N 9,15 | | | | |
| | | | | | | | | | Dipicrate $C_{30}H_{36}N_8O_{12}S$ | 237—239 | N 14,52 | N 14,66 |
| | | | | | | | | | Dihydrochloride $C_{18}H_{32}Cl_2N_2S \cdot H_2O$ | 277—278 | C 53,94; H 8,33; N 7,02 | C 54,39; H 8,62; N 7,05 |
| | | | | | | | | | Monomethiodide**** $C_{19}H_{32}IN_2S$ | 215—219 | C 50,85; H 7,35; I 28,30; N 6,56 | C 50,89; H 7,42; I 28,30; N 6,26 |
| 16 | Morpholine | CH$_2$–CH$_2$ / CH$_2$–CH$_2$ with O | 0,4/0,1 | $C_{16}H_{26}N_2O_2S$ | 74 | M.p. 104—105 from alcohol | C 62,15; H 8,65; S 10,30 | S 10,32 | | | | |
| | | | | | | | | | Dimethiodide $C_{20}H_{36}I_2N_2S$ | 190—193 | C 40,50; H 6,09 | C 40,68; H 6,15 |
| | | | | | | | | | Dipicrate $C_{28}H_{32}N_8O_{16}S$ | 226—230 | N 14,99 | N 14,58 |
| | | | | | | | | | Dihydrochloride $C_{16}H_{28}Cl_2N_2O_2S \cdot H_2O$ | 270 | C 47,68; H 7,48; N 6,22 | C 47,87; H 7,53; N 6,19 |
| | | | | | | | | | Monomethiodide $C_{17}H_{29}IN_2O_2S$ | 153—157 | I 27,22 | I 28,05 |
| | | | | | | | | | Dimethiodide*** $C_{18}H_{32}I_2N_2O_2S$ | 153—157 | C 36,01; H 5,37; S 5,31; N 4,90; I 42,51 | C 36,37; H 5,43; S 5,40; N 4,72; I 42,71 |
| 17 | N-methyl-aniline | R$_1$=CH$_3$, R$_2$=C$_6$H$_5$ | 0,2/0,05 | $C_{22}H_{26}N_2S$ | 87 | M.p. 83—83,5° from alcohol | C 75,14; H 7,57; S 9,17; N 7,97 | C 75,38; H 7,48; S 9,15; N 7,99 | | | | |
| | | | | | | | | | Dipicrate $C_{34}H_{32}N_8O_{14}S$ | 158—159 | N 14,23 | N 13,86 |

*This compound was isolated in an attempt to vacuum-distill the mixture formed as a result of the reaction of (II) with t-butylamine.

**The dried (at 130° in a vacuum) dimethylithiodide did not melt when heated to 360° (in a block).

***Did not melt when heated to 360° in a block.

****Obtained by heating the reactants in benzene; when they were heated in alcohol, the dimethiodide was formed.

## TABLE 2

Products of the Alkylation of Secondary Amines (see Table 1, A) Obtained from BCMDMT

| No. | Amine taken in reaction | $R_1$ | $R_2$ | Formula | Yield (%) | M.p., b.p. (°C) (p in mm) | Found (%) | Calculated (%) | Derivatives Formula | Derivatives M.p. (°C) | Derivatives found, % | Derivatives calc. % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | N,N'-Diisopropyl-2,5-dimethyl-3,4-TBM * | $R_1=CH_3$ | $R_2=i\text{-}C_3H_7$ | $C_{16}H_{30}N_2S$** | 52 | 151—152 (7) | C 67,83; H 10,80; S 11,69 | C 68,03; H 10,63; S 11,34 | Dipicrate $C_{28}H_{40}N_8O_{14}S$<br>Dimethiodide**** $C_{18}H_{36}I_2N_2S \cdot H_2O$ | 193 | N 15,18<br>C 37,37 H 6,55 I 45,78 | N 15,13<br>C 36,98 H 6,82 I 43,49 |
| 2 | N,N'-Diheptyl-2,5-dimethyl-3,4-TBM | $R_1=CH_3$ | $R_2=C_7H_{15}$ | $C_{24}H_{46}N_2S$*** | 70 | 202 (2) | C 73,28; H 11,67; S 8,11; N 7,16; M 390 | C 73,03; H 11,67; S 8,12; N 7,11; M 395 | Dipicrate $C_{36}H_{52}N_8O_{14}S$<br>Dihydrochloride $C_{24}H_{48}Cl_2N_2S$<br>Dimethiodide $C_2 H_{52}I_2N_2S$ | 145—146<br>215—218<br>158—163 | M 842<br>C 61,42 H 10,22<br>C 45,77 H 7,88 N 4,17 I 36,75 | M 853<br>C 61,64 H 10,28<br>C 46,01 H 7,67 N 4,13 I 37,43 |
| 3 | 2,5-Dimethyl-N,N'-di-t-butyl-3,4-TBM | $R_1=CH_3$ | $R_2=C_4H_9$ | $C_{18}H_{34}N_2S$*** | 83 | from alcohol at 37° | C 69,41; H 10,99; S 10,17; N 9,11 | C 69,61; H 11,0'; S 10,32; N 9,02 | Dipicrate $C_{30}H_{40}N_8O_{14}S$<br>Monomethiodide. $C_{19}H_{37}IN_2S$ | 214—215<br>212—215 | N 14,54<br>C 50,17 H 8,13 N 6,30 I 28,59 S 6,82 | N 14,58<br>C 50,43 H 8,24 N 6,19 I 28,09 S 7,09 |

* TBM = thiophenebismethylamine.

** Obtained by alkylation with the aid of methyl benzenesulfonate.

*** Obtained by alkylation with a mixture of formaldehyde and formic acid.

**** Begins to become "wet" at 160°, then darkens, and does not melt when heated in a block to 360°.

experiment with diethylamine in Sections D and E. The absence of data in any given section indicates that in the case under consideration no compound of the particular type was isolated.

The reaction mixture usually consisted of a benzene solution (K) and a precipitate, which was filtered off; it contained hydrochlorides of the amine taken for reaction and the bases formed. The latter were extracted by dissolution of the hydrochlorides in water, rendering the solution alkaline with strong KOH solution, treatment with benzene and ether, and vacuum distillation. In some cases, e.g., in the experiment on the reaction of (II) with isopropylamine, the residue obtained after removal of solvents was treated with a little alcohol; in this way we isolated a reaction product of low solubility in alcohol which was found to be a base of type (IXa) (see Table 1, Section C, No. 10).

In the experiment on the reaction of BCMDMT (II) with heptylamine, solvent was distilled from the mixture of reaction products, and the residue was vacuum-fractionated. In the experiment with aniline the precipitate contained aniline hydrochloride; reaction products were found in the benzene filtrate. Benzene was removed from the benzene filtrate (K); the residue was treated with alcohol or an alcoholic solution of HCl. The treatment with alcohol permitted us to separate reaction products of low solubility in alcohol. In the experiment with aniline such a product was found to be a base of the type (X) (see Table 1, Section B, No. 8), and in the experiment with morpholine a base of the type (VII) (see Table 1, Section E, No. 16).

In the experiment on the reaction of BCMDMT (II) with diethylamine a precipitate of salts did not separate, and after treatment with water and alkali the mixture was extracted with benzene. The latter was vacuum-distilled off, and by recrystallization from alcohol a base of type (V) (see Table 1, Section E, No. 14) was isolated. The alkaline aqueous solution was saturated with potassium carbonate, and extraction with chloroform and removal of the latter in a vacuum gave a compound of type (IXb) (see Table 1, Section D, No. 12). In a similar way, in the experiment on the reaction of (II) with piperidine we isolated a base of type (VII) and a compound of type (IXb) (see description of experiment below).

The methiodides were prepared by heating the bases with excess of methyl iodide in methanol, and in individual cases by heating the reactants in benzene. These salts were recrystallized from alcohol or a mixture of alcohol and water. It was not always possible to determine the decomposition temperature of the methiodide with accuracy as these salts gradually become dark-colored when heated. The capillary containing the substance was usually introduced into a previously heated apparatus. The final decomposition temperature depends on the rate of heating.

The hydrochlorides and picrates were prepared in the usual way, with the exception of the picrates of the bases (IXb), which were prepared by the double decomposition of the hydrochlorides with picric acid. The recrystallization of the hydrochlorides was carried out by their reprecipitation from alcoholic solution with the aid of ether, and the picrates were recrystallized from alcohol*.

## Reaction of 3,4-Bischloromethyl-2,5-dimethylthiophene with Amines

Reaction of Ethylamine with 3,4-Bischloromethyl-2,5-dimethylthiophene. A solution of 35.5 g (0.17 mole) of BCMDMT in 100 ml of benzene was added in small portions to a solution of 34 g (0.75 mole) of ethylamine in 100 ml of dry benzene with cooling in an ice bath. The mixture was kept for four hours surrounded by ice water, and was then left at room temperature for three days; it was then heated in a water bath for three hours. When the mixture was cool, the precipitate that had separated was filtered off; it amounted to 28.2 g, melted over a wide range, and consisted mainly of the hydrochloride of the original ethylamine and, in smaller amount, of the hydrochlorides of the reaction products.

Benzene was distilled off from the benzene filtrate (1), and an oil remained as residue; to this 50 ml of an alcoholic solution of HCl (18%) was added with cooling. The solid mass formed was filtered off, washed with ether, and dissolved in 150 ml of hot water. The solution was cooled, and 50 ml of 40% KOH solution was added. The oil that separated was extracted several times with ether. The combined ether extracts were dried over anhydrous potassium carbonate, and ether was distilled off. The residue partially crystallized out. The solid was filtered off and washed with alcohol. We obtained 10.4 g of substance, m.p. 88-88.5°, and the filtrate (2). After recrystallization from alcohol the melting point did not change [the base (IXa; R = C$_2$H$_5$); for analysis and constants of the salts see Table 1, Section C, No. 9]. Solvent was distilled off from the filtrate (2). The residue was vacuum-fractionated, and at 1.5-2 mm the following fractions were isolated: Fraction I (4.6 g), 108-118°; Fraction II (1 g), 120-156°; Fraction III (5.8 g), 185-205°; Fraction IV (5.5 g), 205-240°.

*The molecular weights of the picrates were determined by the spectrophotometric method [19].

Fraction I was redistilled: the substance (IV; R = $C_2H_5$) came over at 107-115° (2 mm); it crystallized out on standing. The crystals were filtered off and washed with hexane; m.p. 39°. For analysis and constants of the salts see Table 1, Section A, No. 1.

A little alcohol was added to Fraction III of the reaction products, and the mixture was left in a refrigerator. The precipitate that separated was filtered off and amounted to 1.2 g, m.p. 87-88°; it was identical with the already isolated (IXa; R = $C_2H_5$) (see above). Alcohol was distilled from the filtrate, and the residue was vacuum-distilled. At 2 mm a substance (the base X, R = $C_2H_5$) came over at 203-207° as a viscous oil (at 2.5 mm it boiled at 195-197°). For analysis and constants of the salts see Table 1, Section B, No. 6.

In the experiment described (see above) the yields of reaction products were: cyclic base (IXa; R = $C_2H_5$), 39%; diamine (IV; R = $C_2H_5$), 12%; diamine containing two thiophene rings (X; R = $C_2H_5$), 27%. In another experiment carried out under similar conditions the yield of cyclic base (IXa; R = $C_2H_5$) was 27%; that of the diamine (IV) was 25%; and that of the diamine (X; R = $C_2H_5$) was 30%. In an experiment at a 2:1 ratio of ethylamine to BCMDMT a 40% yield of the cyclic base (IXa; R = $C_2H_5$) was obtained; there was 30% of resinous products and 10% of unchanged BCMDMT.

Action of Piperidine on 3,4-Bischloromethyl-2,5-dimethylthiophene. Gradual addition was made of 34 g (0.4 mole) of piperidine to a solution of 21 g (0.1 mole) of BCMDMT in 50 ml of dry benzene. After a few minutes the mixture grew very hot. When the spontaneous evolution of heat had stopped, the mixture was heated at the boil in a water bath for six hours. The precipitate that separated was filtered off and washed with benzene. We obtained a benzene filtrate (A) and a solid (35 g): the latter was dissolved in 50 ml of water. To the solution 50 ml of 40% KOH solution was added. The oil that separated was extracted with benzene. We obtained a benzene extract and an alkaline solution (B). Benzene was distilled from the extract leaving 24.4 g of a solid, which was recrystallized from alcohol. We obtained 21.8 g (71.5%) of 2,5-dimethyl-3,4-bispiperidinomethylthiophene (VII;)

R = $\langle\!\!\begin{array}{c}CH_2-CH_2\\CH_2-CH_2\end{array}\!\!\rangle CH_2$), (71.5%) m.p. 86.5-87°. For analysis and constants of the salts see Table 1, Section E, No. 15.

The alkaline solution (B) (see above) was saturated with potassium carbonate, and the mixture was extracted several times with chloroform. When the latter was distilled off there remained 3.7 g of solid residue, which was washed with a little acetone; it was highly hygroscopic. After recrystallization from acetone we obtained 1.7 g of a substance of m.p. 242° (in a block) which appeared to be 4,5,6,10,11,12-hexahydro-1,3,7,9-tetramethyl-5,11-bispentamethylenedithieno[3,4-c: 3',4'-h][1,6]diazecinium dichloride, of the type (IXb).

Preparation of Bistertiary Amines (VI) from N,N'-Dialkyl-2,5-dimethyl-3,4-thiophene-bismethylamines

a) Action of Methyl Benzenesulfonate. A mixture of 5 g of N,N'-diisopropyl-2,5-dimethyl-3,4-thiophene-bismethylamine and 7 g of methyl benzenesulfonate was heated at 160° in an oil bath for 90 minutes. The dark-colored caramellike mass was dissolved in water, and a 40% solution of KOH was added to the solution. The oil that separated was extracted several times with ether, the ether extract was dried with anhydrous potassium carbonate, and the ether was distilled off. Vacuum distillation of the residue gave 2.9 g (52%) of a substance of b.p. 124° (4 mm). On redistillation N,N'-diisopropyl-N,N',2,5-tetramethyl-3,4-thiophenebismethylamine (VI; $R_1 = C_3H_7$) came over at 151-152° (7 mm). For analysis and constants of the salts see Table 2, No. 1.

b) Action of a Mixture of Formaldehyde and Formic Acid. A mixture of 7.2 g of N,N'-diheptyl-2,5-dimethyl-3,4-thiophenebismethylamine, 4.6 g of formic acid (90%), and 4 ml of 35% aqueous formaldehyde was heated in a water bath for three hours and then left at room temperature overnight. On the next day 2.5 ml of concentrated hydrochloric acid was added to the mixture, and the solution was vacuum-evaporated. The solid residue was dissolved in 17 ml of water, and 10 ml of a 40% solution of KOH was added to the solution. The oil that separated was extracted with benzene. The extract was dried with potassium carbonate, and solvent was distilled from the solution. Vacuum fractionation (2 mm) of the residue gave the following fractions: Fraction I (0.95 g), 184-193°; Fraction II (5.4 g), 194-205°.

Refractionation of Fraction II gave 4.2 g of N,N'-diheptyl-N,N',2,5-tetramethyl-3,4-thiophenebismethylamine (VI; $R_1 = C_7H_{15}$), b.p. 202° (2 mm). For analysis and constants of the salts see Table 2, No. 2.

## SUMMARY

1. The reactions of 3,4-bischloromethyl-2,5-dimethylthiophene with various primary and secondary amines were studied. They resulted in the formation mainly of symmetrical bissecondary and bistertiary amines of structure (IV, (V), and (VII); no compounds analogous in structure to isoindoline were found among the reaction products.

2. Together with the diamines (IV), (V), and (VII), dithienodiazecines of structure (IXa) and (IXb) were obtained.

3. The action of methylating agents on the diamines (IV) gave the corresponding tertiary amines (IV) and their bisquaternary salts.

4. By the action of methyl iodide on the bistertiary amines (V), (VI), and (VII) in methanol, di- and mono-methiodides were formed.

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# RAMAN-SPECTRUM INVESTIGATION OF THE STRUCTURES
## OF SOME 1,2,3-SUBSTITUTED 1,3-BUTADIENES

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By the action of phosphorus pentachloride on 1-buten-3-ynyl ethers with subsequent treatment of the complex formed $[(RO)C(H)-(Cl)-C(H)(PCl_4)-C \equiv CH \cdot PCl_5]$ with sulfur dioxide, Shostakovskii and co-workers obtained compounds of the composition $C_7H_{10}PO_2Cl_3$ and $C_8H_{12}PO_2Cl_3$, which according to the proposed mechanism of the reaction had the formulas: $(H_7C_3O)C(H) = C(POCl_2) - C(Cl) = CH_2$ and $(H_9C_4O)C(H) = C(POCl_2) - C(Cl) = CH_2$. If these formulas are correct, then the compounds, being dienes, may exist in flat transoid (I) and cisoid (II) conformations, i.e., they may show rotational isomerism. As Raman-spectrum data, in agreement with chemical data, show [1] the predominant conformation is undoubtedly the transoid (I) at room temperature. If the compounds investigated are regarded as trisubstituted ethylenes with the substituents $R_1 = OC_3H_7$ or $OC_4H_9$, $R_2 = POCl_2$, and $-C(R_3) \rightleftharpoons CH_2$, it is easy to see that in these compounds geometric isomerism is superimposed on rotational isomerism, so that it may be supposed that each of the compounds investigated exists in the form of four isomers: (III), (IV), (V), and (VI).
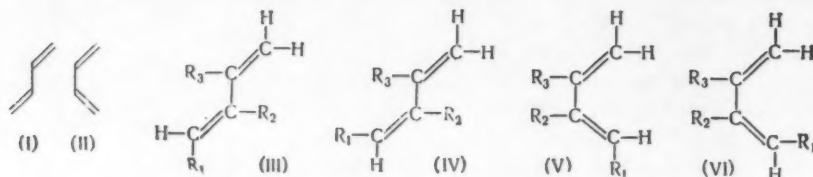


However, as stated above, in diene systems at room temperature transoid conformations, in our case (III) and (IV), undoubtedly predominate. Moreover, in the case of the compounds investigated it must be noted that the cisoid conformations (V) and (VI) will scarcely exist in practice because of steric hindrance due to the large substituents $R_2$ and $R_3$. Hence, at room temperature the compounds investigated probably exist only as transoid (with respect to the $C-C$ bond) conformations (III) and (IV).

However, the transoid isomer (III) is of cis configuration with respect to the relative positions of $R_1$ and $R_2$ in relation to the ethylenic bond, and these groups, being the largest substituents in these compounds, determine the geometric-isomerism terminology; the transoid isomer (IV) is of trans configuration with respect to the relative positions of the same substituents in relation to the ethylenic bond. The isomers (III) and (IV) have no center of symmetry, so that in their Raman spectra (as also in the infrared absorption spectra) frequencies of both forms of vibration of double bonds, symmetrical (s) and antisymmetrical (a) must appear, of these the frequency of the symmetrical vibration is the higher:
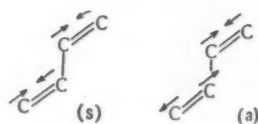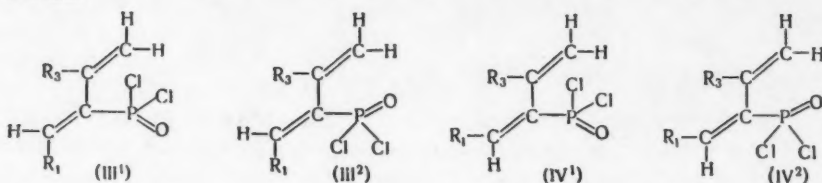
TABLE 1

Frequencies of Symmetrical (s) and Antisymmetrical (a) Vibrations of C=C Double Bonds of the cis and trans Configurations (III) and (IV) of the Transoid Conformation (with respect to the C−C bond) of the Compounds Investigated

| $(H_7C_3O)C(H)=$ $-C(POCl_2)-C(Cl)=CH_2$ | | $(H_9C_4O)C(H)=$ $=C(POCl_2)-C(Cl)=CH_2$ | |
|---|---|---|---|
| cis Configuration (III) | trans Configuration (IV) | cis Configuration (III) | trans Configuration (IV) |
| 1538(a) | 1554(a) | 1543(a) | 1554(a) |
| 1615(s) | 1637(s) | 1618(s) | 1638(s) |

In the Raman spectra of the compounds investigated we did in fact observe frequencies of both forms of double-bond vibrations (table); moreover they are extremely intense and are doublets. The high intensity of these frequencies is characteristic for conjugated C=C double bonds, and their doublet character is to be explained by the presence in the transoid conformation of cis and trans configurations, i.e., the isomers (III) and (IV).

The group $R_2 = POCl_2$ possesses no free rotation because the P=O double bond is in the plane of the conjugated C=C−C=C bonds [2]. This circumstance determines the possibility of cisoid and transoid conformations with respect to the C−P bond: the isomer (III), which is transoid with respect to C−C, has cisoid ($III^1$) and transoid ($III^2$) conformations with respect to C−P; the isomer (IV), which is transoid with respect to C−C, has also cisoid ($IV^1$) and transoid ($IV^2$) conformations with respect to the same C−P bond.



Because of steric factors, of all these isomers the most stable and predominant are probably ($III^2$) and ($IV^2$), but the possibility cannot be excluded of the existence of a certain amount of the isomers ($III^1$) and ($IV^1$); the Raman-spectra data give an indication of this possibility. Because of the considerable difference in the frequencies of C=C and P=O the association of their vibrations is not accompanied by splitting of their frequency into two as a result of the arising of symmetrical and antisymmetrical frequencies, which is characteristic of the case of identical C=C bonds. The differences that we observed in P=O frequencies are probably due to differences in the effects of atoms in the molecule of the P=O bond in the different structures ($III^1$), ($III^2$), ($IV^1$), and ($IV^2$), as complicated by some smearing out of frequencies as a result of conjugation with the C=C bond. In accordance with the above discussion the P=O frequencies should be assigned to the four structures indicated in approximately the following way:

| | ($III^1$) | ($III^2$) | ($IV^1$) | ($IV^2$) |
|---|---|---|---|---|
| $(C_3H_7O)C(H)=C(POCl_2)-C(Cl)=CH_2$ | 1238 (1) | 1249 (9) | 1270 (2) | 1260 (7) |
| $(C_4H_9O)C(H)=C(POCl_2)-C(Cl)=CH_2$ | 1241 (2) | 1251 (3) | 1271 (4) | 1259 (7) |

The vibration frequency of the C−Cl bond in the group −C(Cl) = CH_2 (825 cm$^{-1}$) is the same in all the structures mentioned. This confirms that the compounds investigated have a bond arrangement of the type $R_1$C(H) = C(POCl_2)−C(Cl) = CH_2 and not of the type $R_1$C(H) = C(H)−C(POCl_2) = C(H)Cl, as in the latter case the C−Cl bond would participate in the corresponding cis and trans configurations of trisubstituted ethylenes and would be characterized by two frequencies which are substantially different for these configurations. The vibration frequencies of PCl_2 are in doublets (symmetrical and antisymmetrical vibrations) and are naturally in a lower region of the spectrum, as compared with the frequency of the C−Cl bond: 530 (7 b, db) cm$^{-1}$ in the spectrum of the first compound and 532 (6 b, db) cm$^{-1}$ in the spectrum of the second. The participation of PCl_2, as also that of C−Cl, in the various structures mentioned leads to some smearing out and broadening of the vibration frequencies of these bonds, but not to an increase in the number of frequencies.

Our conclusions concerning the structures of the compounds investigated are confirmed by their chemical behavior: they do not undergo the Diels-Alder reaction either at room temperature, or at about 100°. These reactions could occur if structures (V) and (VI) were present, but the compounds investigated do not exist in these forms.

Below we give the physical constants of the compounds investigated:

| | B.p. in °C (p in mm) | $d_4^{20}$ | $n_D^{20}$ |
|---|---|---|---|
| $(C_3H_7O) C (H)=C (POCl_2)—C (Cl)=CH_2$ | 69—69.5 (0,012) | 1,3152 | 1,5635 |
| $(C_4H_9O) C (H)=C (POCl_2)—C (Cl)=CH_2$ | 82—82,5 (0,02) | 1,3078 | 1,5620 |

The Raman spectra were determined with a Soviet ISP-51 spectrograph with a central camera and on the Hilger E-612 spectrograph with the blue line 4358 A of a mercury lamp as exciting radiation*.

$(C_3H_7O)C(H) = C(POCl_2) - C(Cl) = CH_2$, $\Delta \nu$, cm$^{-1}$ :

161 (6* sh), 172(3*), 184(1*), 199(1*), 209(1*), 239(2* *) − 250(5* *) − 263(5* *) 274(4* *) − 294(1* *) band, 312(1*), 324 (2*), 362 (2 db), 395 (5 db), 442 (0 db), 491 (0 db), 530 (7 b, db), 563 (0), 591 (0), 635 (0 db), 738 (0), 751 (3), 775 (0), 825 (10 db*), 839 (2*), 929 (2* *), 942 (2* *), 952 (2* *), 978 (0), 1023 (0), 1093 (0*), 1104 (4*), 1114 (3*), 1144 (2* *), 1156 (2 * *), 1188 (3*), 1198 (3*), 1206 (6*), 1219 (6*), 1238 (1* *), 1249 (9* *), 1260 (7* *), 1270 (2* *), 1293(3* db) − 1320(2*) − 1337(5* db) − 1352(1*) band, 1381(1), 1394(3), 1467(3), 1538(10*), 1554(10*), 1615 (10* *), 1637 (10* *), 2876 (3*), 2905 (0*), 2930 (3*), 2944 (3*), 2972 (2*), 3023 (0* *), 3056 (2* *), 3143 (0*) 3153 (1*), 3176 (0*).

$(C_4H_9O)C(H) = C(POCl_2) - C(Cl) = CH_2$, $\Delta \nu$, cm$^{-1}$ :

160 (6* sh), 171 (3*), 183 (1*), 198 (1*), 211 (1*), 237 (2* *) − 249 (3* *) − 260 (3* *) − 277 (3* *) − 286 (1* *) band, 314 (0*), 326 (1*), 358 (2 db), 394 (3 db), 457 (0 db), 496 (0 db), 532 (6 b, db), 562 (0), 588 (0), 640 (0 db), 745 (0), 756 (3), 778 (0), 824 (8 b*), 840 (1*), 855 (1*), 928 (2* *), 938 (2* *), 948 (2* *), 979 (0), 1023 (0), 1094 (1*), 1105 (4*), 1116 (3*), 1144 (2* *), 1156 (2* *), 1169 (0* *), 1185 (2*), 1195 (3*), 1209 (7*), 1219 (3*), 1241 (2* *), 1251 (3 sh*), 1259 (7** sh), 1271 (4 sh* *), 1293 (3* db) − 1317 (2* db) − 1329 (5*) − 1343 (5*) band, 1376 (1* *), 1394 (3* * db), 1468 (3), 1543 (10*), 1554 (10*), 1618 (10* *), 1638 (10* *), 2883 (4* db), 2903 (2 sh*) 2913 (4*), 2926 (2* sh), 2936 (4*), 2959 (1*), 2978 (0*), 3030 (1* *), 3063 (3* *), 3112 (0), 3150 (1*), 3170 (3*).

## SUMMARY

In the compounds investigated, namely 3-chloro-2-(dichlorophosphinyl)-1-propoxy-1,3-butadiene and 1-butoxy-3-chloro-2-(dichlorophosphinyl)-1,3-butadiene [1-(alkoxymethylene)-2-chloroallylphosphonic dichlorides], there is superposition of rotational isomerism at single C−C and C−P bonds on geometric isomerism at the C=C double bond adjacent to the C−P bond. As a result of this and of some steric hindrance, the compounds investigated exist mainly in the form of the isomers (III$^2$) and (IV$^2$) and to a less extent in the form of (III$^1$) and (IV$^1$) with a flat arrangement of the three double bonds.

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*The symbols given in the intensities are: b, broad line; sh, sharp line; asterisks denote lines on a background which is held in common with neighboring lines marked with the same number of asterisks.

# "SYNTHESIS OF THE VINYL ESTER OF PHTHALYLGLYCINE AND SOME OF ITS TRANSFORMATIONS"

M. F. Shostakovskii and E. S. Shapiro

During the past decade, investigation of the reactions of polymerization of anhydrides of N-carboxy-$\alpha$-amino acids has acquired considerable importance. The synthetic polymers obtained by this method consist of acid residues connected to each other by peptide links. It appears that unsaturated compounds derived from $\alpha$-amino acids are of great interest, specifically the vinyl esters of these acids, which may become starting materials for novel polymers.

We have developed a method for the direct vinylation of N-substituted $\alpha$-amino acids; phthalylglycine has been chosen as a model. The reaction was carried out with a large excess of acetylene and with the use of dry and pure dioxane as a solvent, i.e., under conditions which had been repeatedly used with success in our laboratory [1, 2]. As a catalyst anhydrous zinc acetate was applied; the vinyl ester in question was synthesized with a yield of 80-85%. The information published in the literature is limited to one patent [3], in which a method for the preparation of vinyl esters of some N-acetyl-$\alpha$-amino acids is recommended that involves treatment of these acids in an evacuated (down to 5 mm of pressure) autoclave in the presence of mercury compounds [$HgSO_4$, $Hg_3(PO_4)_2$, HgO] and carrying out the reaction in certain solvents. The yields obtained were very small; no constants or analytical results were

reported. The vinyl ester of phthalylglycine $C_6H_4\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle NCH_2COOCH=CH_2$ — synthesized by us was found to be a

crystalline substance that dissolves easily in the majority of organic solvents but is not soluble in petroleum ether or water. The last circumstance was taken advantage of for the purification of the vinyl ester from the initial phthalylglycine in those experiments in which the reaction of vinylation did not proceed quantitatively. Some reactions of the vinyl ester obtained were investigated. Thus, it was found that its hydrolysis required somewhat more stringent conditions than those which were effective in the case of vinyl alkyl ethers: heating to 80° with 15% sulfuric acid was necessary. Addition of thiols took place smoothly when the reaction was catalyzed by an initiator of radical reactions. The corresponding sulfides were formed:

$$C_6H_4\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle NCH_2COOCH=CH_2 + RSH \rightarrow C_6H_4\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle NCH_2COOCH_2CH_2SR$$
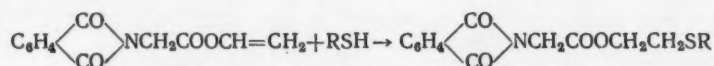
In the presence of the dinitrile of azoisobutyric acid or of benzoyl peroxide, the vinyl ester of phthalylglycine polymerized. The possibility of copolymerizing it with methyl methacrylate has been demonstrated in principle.

## EXPERIMENTAL

Phthalylglycine was prepared by known methods [4-6]; its m. pt. was 191-192°.

Vinylation was carried out in a rotating autoclave equipped with a pressure gauge and a thermocouple by means of which the temperature would be controlled automatically.

Into a 1.5 liter autoclave were placed 10 gr. of phthalylglycine, 0.4 gr. of anhydrous zinc acetate, and 50 ml of pure and dry dioxane. The air was displaced with nitrogen and the nitrogen with acetylene. The latter was introduced 3-4 times into the autoclave from a cylinder, the pressure in which was no lower than 13-14 atm. The total quantity of acetylene comprised 16.3 gr, i.e., 12M per 1M of phthalylglycine. Heating was carried out for 8 hours at

170°. After filtration and removal of the solvent by distillation in vacuum the weight of the dry product amounted to 9.9 gr (87% of theory); m. pt. 105-107°. Additional purification of the product was carried out by recrystallization from 50% alcohol — for the first time in the presence of wood charcoal and then twice in its absence. The vinyl ester of phthalylglycine crystallized in brilliant platelets with a m. pt. of 107.5-108°. Found: C 62.11; H 3.85; N 5.97%. $C_{12}H_9NO_4$. Calculated: C 62.34; H 3.92; N 6.06%.

TABLE 1. Vinylation of Phthalylglycine

| No. of the experiment | Acetylene in M/1M of phthalyl-glycine | Tempera-ture, °C | Time in hours | Yield of reaction products, % of theory | |
|---|---|---|---|---|---|
| | | | | initial product | vinyl ester |
| 7 | 9 | 160 | 8 | 60,3 | 8,9 |
| 8 | 10 | 160 | 10,5 | 73,5 | 8 |
| 9 | 10 | 170 | 6 | — | 74,6 |
| 21 | 10 | 170 | 7,0 | — | 87,2 |
| 15 | 9,5 | 170 | 8 | — | 88,1 |
| 27 | 12 | 170 | 7 | — | 83,8 |
| 17* | 8 | 170 | 6,5 | 28 | 24,2 |
| 19* | 8 | 170 | 8 | 20 | 44,3 |

*In experiments 17 and 19 the initial pressure of acetylene was 11-12 atms. and its excess was only 8 molar — as a result of this a mixture of products was obtained and unavoidable losses resulted during recrystallization.

In Table 1 some experiments of the vinylation of phthalylglycine under different conditions are summarized. The weight of phthalylglycine used in a single experiment amounted to 5-15 gr; 5 ml of dioxane per 1 gr of phthalylglycine were used; the amount of zinc acetate comprised 4% by weight of the phthalylglycine.

Hydrolysis of the vinyl ester of phthalylglycine was carried out in an apparatus equipped with an agitator, a tube for introducing nitrogen, and a tube for conducting away acetaldehyde to a battery of cooled traps. Into the reaction flask with a capacity of 100 ml, 0.54 gr of ether and 20 ml of 15% $H_2SO_4$ were introduced. Heating was carried out on a water bath at 78-82° for 4 hours under agitation; the acetaldehyde was blown out by a moderately fast current of nitrogen. Titration with bisulfite established that 0.097 gr of acetaldehyde (calculated 0.1028 gr) were present, i.e., 94% of theory. After filtration, washing, and drying, the residue consisted of a crystalline product with a m. pt. of 188-190°. Its weight was 0.46 gr (96% of theory). After a single recrystallization from boiling water, m. pt. 191-192°; the m. pt. of a sample mixed with authentic phthalylglycine did not show any depression.

Addition of thiols. A weighed quantity of ether (3-4 gr) in 10-12 ml of dioxane, a bimolar excess of the appropriate thiol, and 0.5% by weight of the dinitrile of azoisobutyric acid were placed into a tube which was sealed under cooling. Heating was then carried out for 18 hours at 75-80°.

For the synthesis of the β-ethylthioethyl ester of phthalylglycine 4 gr of the vinyl ester of phthalylglycine were reacted. After elimination of the excess of the thiol and of dioxane, the reaction product was distilled in vacuum; m. pt. 139-141° (0.015 mm); 4.1 gr; $n_D^{26}$ 1.5602. Found: C 57.26; H 5.08; S 10.34%. $C_{14}H_{15}O_4NS$. Calculated: C 57.32; H 5.15; S 10.29%.

TABLE 2. Yield and Solubility of the Polymer

| Initiator | Yield of the polymer, % | N. % | | Solubility | | | | |
|---|---|---|---|---|---|---|---|---|
| | | found | calcd. | ace-tone | ben-zene | alco-hol | ether | dioxane |
| Dinitrile of azo-isobutyric acid | 40 | 5,96 | 6,06 | — | — | — | — | + |
| Benzoyl per-oxide | 70 | 5,77 | 6,06 | — | — | — | — | + |

For the synthesis of the β-butylthioethyl ester of phthalylglycine 3 gr of the vinyl ester were reacted. On distillation in vacuum 3.2 gr of an ester with a b.p. of 150-152° (0.008 mm) were obtained. Found: C 59.72; H 5.88; S 9.78%. $C_{16}H_{19}O_4NS$. Calculated: C 59.79; H 5.96; S 9.98%. After distillation both sulfides were almost colorless and highly viscous liquids which crystallized on standing. After recrystallization from petroleum ether the m. pts. of the esters were 43° and 37-38°, respectively.

Polymerization and copolymerization of the vinyl ester of phthalylglycine were carried out in sealed glass tubes in the presence of 5% by weight of the initiator. The contents of the tubes were heated for 14 hours at 100°. The solvent consisted of 2 gr. of ether in 20 ml of dioxane. For the dioxane solution the polymer and copolymer were precipitated with ether. The products were white amorphous substances (see Tables 2 and 3).

TABLE 3. Copolymerization in the Presence of the Dinitrile of Azoisobutyric Acid ($M_1$ — methyl methacrylate; $M_2$ — vinyl ester of phthalylglycine)

| Molar fraction in the initial mixture | | Yield of the copolymer in % of the weight of the monomers reacted | Composition of the copolymer | |
|---|---|---|---|---|
| $M_1$ | $M_2$ | | N found in the copolymer, % | molar fraction of $M_2$, % |
| 50 | 50 | 17 | 2,83 | 27,5 |

The copolymer was dissolved in acetone and reprecipitated with methanol.

## SUMMARY

1. A method has been evolved for the synthesis of the vinyl ester of phthalylglycine.

2. Some transformations of the vinyl ester of phthalylglycine have been investigated including its hydrolysis, the addition of thiols to it, and (preliminarily) its polymerization and copolymerization with methyl methacrylate.

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# "OXIDATION OF DIALCOHOLCELLULOSE WITH NITROGEN OXIDES"

N. Ya. Lenshina, V. S. Ivanova, and V. I. Ivanov

It was demonstrated in previous work done by us [1-3] that oxidation with nitrogen oxides of the primary hydroxyl groups in open fragments of the types (II) and (III) practically did not take place under the conditions in question.
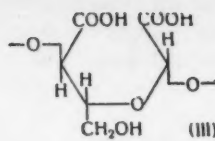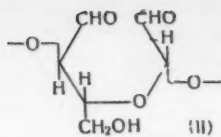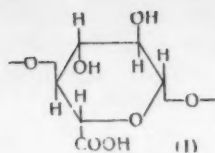
The assumption was made that the oxidation of primary OH groups at $C_6$ may be affected by the condition of the functional groups IIa and IIIa, where the primary OH group is blocked, and by the opening of the glucopyranoside ring (II and III).
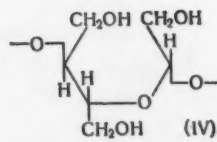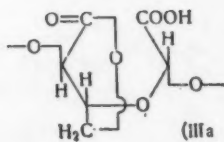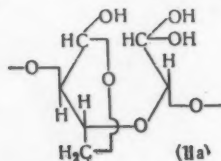


The present communication reports data on the oxidation with nitrogen oxides of derivatives of the structure (IV), which are conventionally referred to in the literature as dialcoholcellulose.

## EXPERIMENTAL

The initial preparations were obtained by applying method described in the literature [4]. Oxidation with the nitrogen oxides of the samples under investigation was carried out under standard conditions at 20° by reacting for 6-48 hours. The velocity of oxidation of preparations having the constitution (IV) was estimated on the basis of the number of carboxyl groups (total number and the number of uronic groups). Figures 1 and 2 show curves which indicate the velocity of oxidation of the preparations investigated. Curves 1 on these figures indicate that after 24 hours oxidation practically stopped.
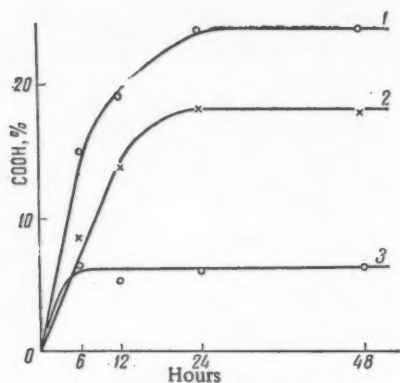


Fig. 1. Oxidation with nitrogen oxides of dialcoholcellulose sample No. 38: 1) Total content of carboxyl groups; 2) content of uronic carboxyl groups; 3) content of non-uronic carboxyl groups.
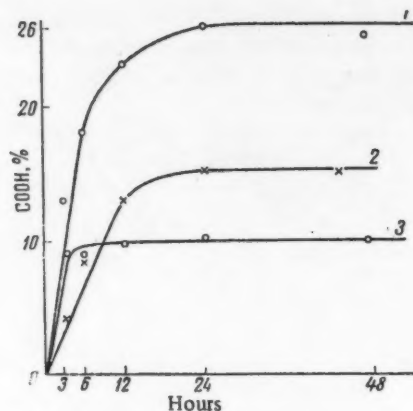
Fig. 2. Oxidation with nitrogen oxides of dialcoholcellulose sample No. 39 (the curves represent the same data as those listed in the caption under Figure 1).

The process of oxidation takes place mainly under formation of links of the structure (I), which is confirmed by the curves expressing the increase of uronic carboxyl groups (the curves 2, in Figs. 1 and 2). The type of increase of the number of non-uronic carboxyl groups, which is expressed by curves 3 in Figs. 1, and 2, corresponds to their increase due to the oxidation of aldehyde groups (there is a non-linear relation). The table lists data concerning the content of carboxyl groups after oxidation with nitrogen oxides of dialcoholcellulose preparations containing in the macromolecule different quantities of links having the structure (IV).

Content of Carboxyl Groups in Dialcoholcellulose Preparations Oxidized
with Nitrogen Oxide for 24 Hours

| No. of the sample | Content of COOH groups, % | | | | |
|---|---|---|---|---|---|
| | total | uronic | | non-uronic | |
| | | calculated* | found | calculated** | found |
| 1 | 2 | 3 | 4 | 5 | 6 |
| 38 | 24,0 | 19,2 | 18,0 | 6,3 | 6,0 |
| 39 | 26,0 | 15,7 | 15,5 | 10,6 | 10,5 |
| 32 | 28,0 | 12,3 | 15,0 | 14,0 | 13,0 |

*Quantity of uronic carboxyl groups calculated on the basis of the number
of anhydroglucose units.
* *Quantity of carboxyl groups calculated on the basis of glycolic acid
obtained by hydrolysis of (IV).

It follows from the data listed in the table that the quantity of uronic carboxyl groups corresponded to the quantity calculated (columns 3 and 4). These results indicate that the uronic carboxyl groups form part of the structure (I). To clarify the chemistry of the process involved, we took into consideration that under conditions of oxidation with nitrogen oxides the structure (IV) undergoes hydrolytic decomposition with the formation of glycolic aldehyde [5]. The latter oxidizes rapidly to glycolic acid, the presence of which we established chromatographically [6]. Furthermore, the data listed in the table indicate that the content of carboxyl groups calculated on the basis of glycolic acid corresponds to the quantity actually found. On the basis of these data the course of the chemical re- actions taking place under the action of nitrogen oxides on the structure (IV) can be represented by the scheme:



Consequently, under the conditions in question there was no oxidation of primary OH groups in the structure (V) or oxidation of glycolic acid into oxalic acid. This is in agreement with data on the oxidation of ethylene glycol and other aliphatic carbinols with nitrogen oxides [7]. Our earlier work on the oxidation 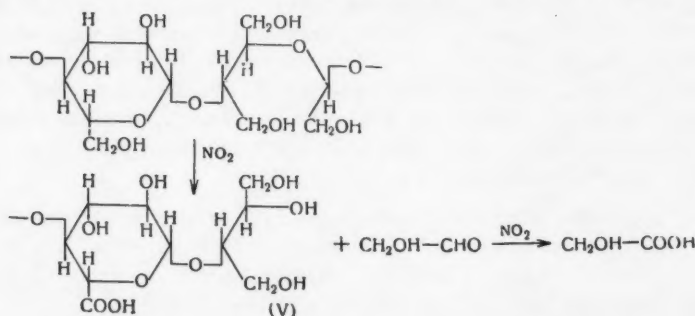of preparations of the structures (II) and (III) with nitrogen oxides indicated that oxidation of the OH group at $C_6$ was strongly inhibited in them [2, 3]. Oxidation of $C_6$ in preparations of the structure (IV) under the conditions in question for all practical purposes also did not take place. On the basis of the results obtained, one may conclude that the strong inhibition of the oxidation of the OH group at $C_6$ in the open glucopyranoside ring is caused not so much by the condition of the functional groups (IIa and IIIa), as by the opening of the ring. The data obtained lead to the conclusion that the preferential oxidation by nitrogen oxides of the OH groups at $C_6$ to carboxyl groups (structure I) in glucosides and polysaccharides is due to the presence of, and inherent properties of, the glucopyranoside ring.

SUMMARY

1. The oxidation with nitrogen oxides of primary hydroxyl groups in the open glucopyranoside ring of the cellulose macromolecule was investigated. The typical reaction of the oxidation of the primary hydroxyl groups in the anhydroglucose unit is inhibited to a considerable extent in open glucopyranoside rings.

2. The selective oxidation with nitrogen oxides of the OH group at $C_6$ in the cellulose molecule is due to the presence and nature of the glucopyranoside ring.

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# "CONDENSATION OF PIPERYLENE WITH NITROOLEFINS"

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In the preceeding article we described the condensation of mono- and disubstituted nitroolefins with butadiene [1]. The present report deals with the interaction of some mono- and disubstituted nitroolefins with piperylene. Only two articles were available in the literature in regard to the condensation of piperylene with nitroolefins at the time when our work was begun. One of these articles described the preparation of addition products derived from piperylene and 1-nitropentene [2], 2-($\alpha$-furyl)nitroethylene [2], or $\beta$-nitrostyrene [2, 3]. When the experimental work of the investigation reported by us in this instance was completed an article appeared which described the condensation of piperylene with $\beta$-trichloromethylnitroethylene [4].

We investigated the interaction of piperylene with mono-substituted dienophilic nitro compounds (nitroethylene and 1-nitropropylene-2) and di-substituted dienophilic nitro compounds (1-nitropropylene-1,$\beta$-dichloromethylnitroethylene, and the methyl ester of $\beta$-nitroacrylic acid). On heating of a mixture of nitroethylene with piperylene in benzene for 11 hours, the addition product was obtained with a yield of 89-91%.
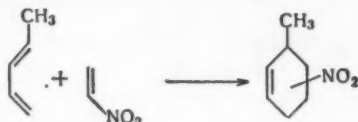


As was to be expected, 1-nitropropylene-2 condenses with much greater difficulty with piperylene: after a mixture of the reacting substances was heated in a sealed tube for 26 hours at 100°, the addition product formed with a yield of only 18%.
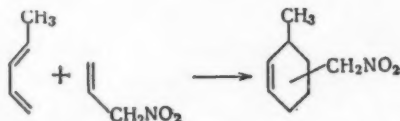


Heating of a mixture of piperylene with 1-nitropropylene-1 in a sealed tube for 12 hours at 100° resulted in the formation of the addition product with a yield of 55%. Under analogous conditions

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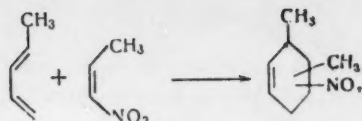
(time of the reaction 12 hours) the yield of the addition product from piperylene and β-trichloromethylnitroethylene reached 81%
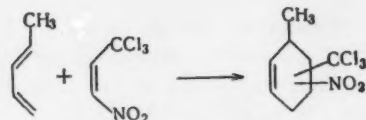


Heating of piperylene with the methyl ester of β-nitroacrylic acid in a sealed tube for 12 hours at 110° resulted in formation of the addition product with a yield of 85%.
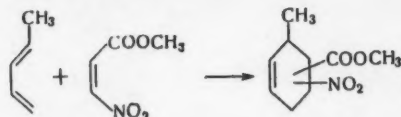


When the condensation of piperylene with di-substituted dienophilic nitro compounds was carried out in a chlorobenzene solution at 100° for 38 hrs, the yields of the addition products comprised 50-60%.

## EXPERIMENTAL

Trans-piperylene with b.p. of 41-42°; $n^{20}D$ 1.4320 [5] was used in all syntheses.

Condensation with nitroethylene. A solution of 30 gr (0.41 M) of nitroethylene and 54.4 gr (0.8 M) of piperylene in 100 ml of dry and pure benzene was boiled under reflux for 7 hrs. To prevent polymerization, pyrogallol was added. The yield was 53.1 gr (approx. 91% of theory) of 3-methyl-4(5)-nitrocyclohexene-1 with b.p. of 93-93.5° (8 mm); $n^{20}D$ 1.4798; $d^{20}_4$ 1.0751. Found: C 59.55; 59.40; H 8.02; 8.05; N 9.95; 9.99%. $C_7H_{11}NO_2$. Calculated: C 59.57; H 7.80; N 9.93%.

Condensation with 1-nitropropylene-2. A mixture of 4 gr (0.046 M) of freshly distilled 1-nitropropylene-2, 4.7 gr (0.069 M) of piperylene, and a small quantity of pyrogallol was heated in a sealed tube for 26 hours at 100°. The yield was 1.3 gr of 3-methyl-4(5)-nitromethylcyclohexene-1 (18% of theory) with b.p. of 63° (1 mm); $n^{20}D$ 1.4731; $d^{20}_4$ 1.0371. Found: C 61.45; 61.43; H 8.21; 8.47; N 9.38; 9.44%. $C_8H_{13}NO_2$. Calculated: C 61.93; H 8.38; N 9.03%.

Condensation with 1-nitropropylene-1. A mixture of 2.3 gr (0.025 M) of 1-nitroprolylene-1, 3.4 gr (0.05 M) of piperylene, and a small quantity of pyrogallol were heated in a sealed tube at 100° for 12 hours. The yield was 2.2 gr (55% of theory) of 3,5(4)-dimethyl-4(5)-nitrocyclohexene-1 with a b.pt. of 84-85.5° (8 mm); $n^{20}D$ 1.4719; $d^{20}_4$ 1.0465. Found: C 61.71; 61.66; H 8.49; 8.50; N 9.03; 9.26%. $C_8H_{13}NO_2$. Calculated: C 61.93; H 8.38; N 9.03%.

Condensation with the methyl ester of β-nitroacrylic acid. A mixture of 4.8 gr (0.036 M) of the methyl ester of β-nitroacrylic acid, 2 gr (0.07 M) of piperylene, and a small quantity of pyrogallol was heated in a sealed tube for 12 hours at 110°. The resulting yield was 4.95 gr (85% of theory) of 3-methyl-4(5)-nitro-5(4)-carbomethoxycyclohexene-1 with b.pt. of 108-108.5° (1 mm); $n^{20}D$ 1.4795; $d^{20}_4$ 1.1819. Found: C 54.28; 54.42; H 6.51; 6.58; N 6.64; 6.54%. $C_9H_{13}NO_4$. Calculated: C 54.32; H 6.53; N 7.03%.

Condensation with β-trichloromethylnitroethylene. A mixture of 5.15 gr (0.027 M) of β-trichloromethylnitro-ethylene, 3.67 gr (0.054 M) piperylene, and a small quantity of pyrogallol were heated in a sealed tube for 12 hours at 100°. The resulting yield of 3-methyl-4(5)-nitro-5(4)-trichloromethylcyclohexene-1 amounted to 5.65 gr (81% of theory); b.pt. 134-135° (2 mm); $n^{20}D$ 1.5246. On melting the substance crystallized; m.pt. 60-61°. Found: C 37.28; H 3.85; Cl 41.19; 41.09; 41.42%. $C_8H_{10}NO_2Cl_3$. Calculated: C 37.13; H 3.86; Cl 41.19%. According to data published in the literature [5], the b.pt. is 110-111.5° (1 mm); $n^{20}D$ 1.5232.

## SUMMARY

The condensation of piperylene with nitroethylene, 1-nitropropylene-2, 1-nitropropylene-1, β-trichloromethyl-nitroethylene, and the methyl ester of β-nitroacrylic acid was investigated. The corresponding addition products were prepared.

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## "CONDENSATION OF BUTADIENE WITH NITROOLEFINS"

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In prior work we investigated the condensation of mono- and disubstituted nitroolefins with cyclic dienes [1, 2]. It appeared of interest to investigate the interaction of same nitroolefins with non-cyclic dienes. We used butadiene as a diene in this case.

Reports published in the literature describe the condensation of butadiene with 1-nitropentene-1 [3], 2-nitro-butylene-1 [4], 2-(α-thienyl)nitroethylene [4], β-nitrostyrene [5, 6], and homologs and derivatives of β-nitrostyrene [7-9]. The reaction was carried out by heating the ingredients for many hours in an autoclave or in a sealed tube. We brought about the diene condensation of butadiene with nitroethylene, nitropropylene, β-nitrostyrene, β-trichloro-methylnitroethylene, and the methyl ester of β-nitroacrylic acid under similar conditions. All reactions were carried out by heating a mixture of the components in sealed glass tubes on a boiling water bath for 38 hours. The sole exception was the reaction of butadiene with nitroethylene: in this case the mixture was heated for 11 hours at 60-65°. Nitroethylene reacted particularly smoothly with butadiene. When this condensation was carried out in a sealed tube, the yield of 4-nitrocyclohexene-1 amounted to 74%; when the reaction was carried out in a rotating autoclave the yield could be raised to 95%.



A somewhat lower yield (68%) of the addition product resulted when butadiene and methyl ester of β-nitro-acrylic acid which had been dissolved in chlorobenzene were heated in a sealed tube:
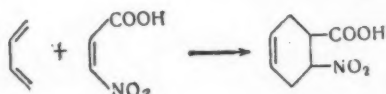


The remaining three olefins, i.e., 1-nitropropylene-1, β-trichloromethylnitroethylene, and β-nitrostyrene, reacted under the same conditions with butadiene, giving yields of the addition products amounting to 42-55%:

$$\text{\Huge $\langle\!\langle$} \quad + \quad \text{\Huge $\langle\!\langle$}_{\text{NO}_2}^{\text{R}} \quad \longrightarrow \quad \text{\Large $\bigcirc$}_{\text{NO}_2}^{\text{R}}$$

$$R = CH_3 \, , CCl_3 \, , \, C_6H_5$$
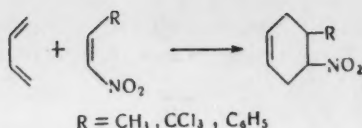
While the work described was in progress an article [10] appeared in which the preparation of an addition product from butadiene and β-trichloromethylnitroethylene was described.

## EXPERIMENTAL

4-Nitrocyclohexene-1. a) A mixture of 39.55 gr (0.54 M) of nitroethylene, 54 gr (1.0M) of butadiene, and a small quantity of pyrogallol, which had been dissolved in 100 ml of pure and dry chlorobenzene, was heated in a rotating autoclave at 60-65° for 11 hours. After completion of the reaction the solvent was distilled off and the residue subjected to fractional distillation in vacuum. The product consisted of 65 gr (approx. 95% of theory) of 4-nitrocyclohexene-1 with b. pt. 63-64° (2 mm); $n^{20}D$ 1.4868; $d^{20}_4$ 1.1168; Found MR 32.69; calculated MR 32.93. Found: C 56.65; 56.93; H 7.23; 6.98; N 11.00; 10.63%. $C_6H_9NO_2$. Calculated: C 56.69; H 7.08; N 11.02%. b) A mixture of 5 gr (0.068 M) of nitroethylene, 10 gr (0.18 M) of butadiene, a small quantity of pyrogallol and 20 ml of pure and dry chlorobenzene was sealed in a glass tube. The glass tube was placed in a protective steel jacket and heated for 11 hours at a temperature of the bath equal to 60°. After completion of the reaction the glass tube was cooled and opened. The solvent was distilled off and the residue fractionated in vacuum. The yield of 4-nitrocyclo-hexene-1 amounted to 6.47 gr (74% of theory). The product had a b. pt. of 63-64° (2 mm). In all other preparations a mixture of the diene and the dienophilic nitro compound was heated in a sealed glass tube placed into a boiling water bath; the heating was continued for 38 hours.

4-Nitro-5-methylcyclohexene-1. By reacting a mixture of 4.35 gr (0.05M) of 1-nitropropylene-1 with 5.4 gr (0.1M) of butadiene in the presence of a small quantity of pyrogallol in 10 ml of dry and pure chlorobenzene 3.7 gr (53% of theory) of 4-nitro-5-methylcyclohexene-1 were obtained; b. pt. 87° (13 mm); $n^{20}D$ 1.4742; $d^{20}_4$ 1.0646; found MR 37.22; calculated MR 37.58. Found: C 59.21; 59.05; H 7.89; 8.02; N 9.53; 9.77%. $C_7H_{11}NO_2$. Calculated: C 59.57; H 7.80; N 9.92%.

4-Nitro-5-phenylcyclohexene-1. From a mixture of 2.98 gr (0.02M) of β-nitrostyrene and 2.16 gr (0.04 M) of butadiene to which a small quantity of pyrogallol had been added and which was dissolved in 10 ml of dry and pure chlorobenzene, 1.73 gr (42% of theory) of 4-nitro-5-phenylcyclohexene-1 with m. pt. of 103-104° were obtained. Data published in the literature [6]: m. pt. 103-104°.

4-Nitro-5-carbomethoxycyclohexene-1. From a mixture of 4.9 gr (0.037M) of methyl ester of β-nitroacrylic acid and 3.78 gr (0.07M) of butadiene to which a small quantity of pyrogallol had been added and which was dissolved in 10 ml of pure and dry chlorobenzene, 4.6 gr (68% of theory) of 4-nitro-5-carboxymethoxycyclohexene-1 with b. pt. of 117° (2 mm) were obtained. The substance crystallized on standing; m. pt. 29-30°. Found: C 51.82; 51.80; H 5.92; 5.94; N 7.31; 7.24%. $C_8H_{11}O_4N$. Calculated: C 51.89; H 5.94; N 7.56%.

4-Nitro-5-trichloromethylcyclohexene-1. From a mixture of 1.9 gr (0.01M) of β-trichloromethylnitroethylene and 1.08 gr (0.02M) of butadiene to which a small quantity of pyrogallol had been added and which was dissolved in 10 ml of pure and dry chlorobenzene, 4-nitro-5-trichloromethylcyclohexene-1 was obtained with a yield of 1.35 gr (55.5% of theory): b. pt. 134-135° (2 mm); $n^{20}D$ 1.5330; $d^{20}_4$ 1.4630; found MR 51.87; calculated MR 52.03. Found: C 34.34; 34.24; H 3.27; 3.08; Cl 43.43; 43.32%. $C_7H_8NO_2Cl_3$. Calculated: C 34.35; H 3.27; Cl 43.55%.

## SUMMARY

The diene condensation of butadiene with some dienophilic nitro compounds was investigated. The addition products which formed were prepared for the first time.

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# "CATALYTIC DEHYDROCYCLIZATION OF DIETHYLAMINE WITH THE FORMATION OF A FIVE-MEMBERED HETEROCYCLIC RING"

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We demonstrated in earlier work [1] that at 310° in the presence of platinized carbon paraffins, alkyl benzenes, and alkyl cyclopentenes undergo a $C_5$-dehydrocyclization, i.e., their straight hydrocarbon chain closes, forming a five-membered ring. It appeared of interest to establish whether this reaction is restricted to hydrocarbons or whether compounds of a different composition may also undergo the same transformation — for instance, compounds containing hetero-atoms in the straight chain, such as dialkylamines. In the case of compounds of this type one might expect that formation of a new C—C bond would lead to pyrrolidines
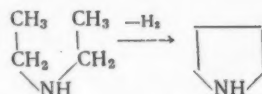


or products resulting from subsequent transformations of the pyrrolidines. To find the answer to this question, we conducted diethylamine over platinized carbon. We found that there was a considerable amount of decomposition and that the yield of liquid catalyzate amounted to only 30%. Investigation of this catalyzate by gas-liquid chromatography showed that it had a complex composition: the chromatogram contained nine peaks (Fig. 1), some of which could be identified by adding to the catalyzate small quantities of the reaction products expected and observing the increase in the area of the corresponding peak (see, for instance, Fig. 2). In this manner it was possible to demonstrate the presence in the catalyzate of pyrrole and of significant quantities of butylamine and acetonitrile. The presence of pyrrolidine could not be established, although it is not out of the question that this substance was present. No separate peak corresponding to pyrrolidine was found. However, a special experiment showed that in chromatography with the use of the liquid stationary phase applied by us acetonitrile and pyrrolidine could not be separated. One must further emphasize that under the conditions of our experiments, pyrrolidine would have been capable of undergoing further reactions. Thus, Zelinskii and Yur'ev [2] established that at 300° pyrrolidine is dehydrogenated to pyrrole on palladium, while Yur'ev and Shen'yan [3] found that under much milder conditions than those applied in our experiments hydrogenolysis of the pyrrolidine ring takes place in a hydrogen atmosphere with the formation of amines. In addition to the dehydrocyclization of diethylamine and the dehydrogenation of pyrrolidine, the process of the formation of acetonitrile

$$CH_3CH_2NHCH_2CH_3 \xrightarrow{-C_2H_4} CH_2CH_2NH_2 \xrightarrow{-2H_2} CH_3CN$$
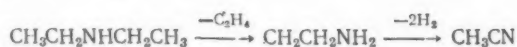
could have served as a source of hydrogen in our experiments.
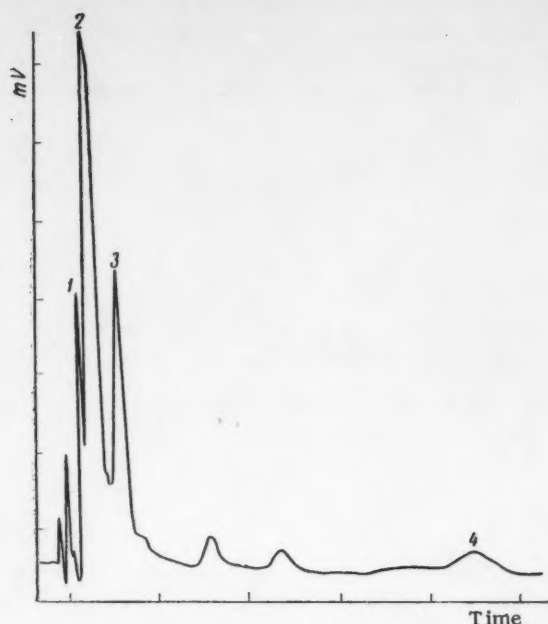
Fig. 1. Chromatogram of the catalyzate: 1) diethyl-amine; 2) acetonitrile; 3) n-butylamine; 4) pyrrole.
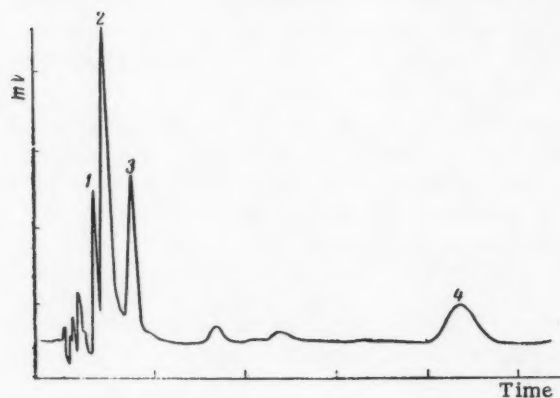


Fig. 2. Chromatogram of catalyzate to which pyrrole and diethylamine had been added: 1) diethylamine; 2) acetonitrile; 3) n-butylamine; 4) pyrrole.

The reaction formulated above has been found to take place in the presence of nickel and copper [4]. One half of the hydrogen formed in the course of the reaction would have served for the hydrogenation of ethylene to ethane* while the remaining hydrogen would have been used up in the hydrogenolysis of pyrrolidine. Apparently the reaction scheme of the transformation of diethyl amine was as follows:

$$CH_3CH_2 + CH_3CN \xleftarrow{-H_2} \underset{NH}{CH_2 \quad CH_2} \overset{CH_3 \quad CH_3}{\phantom{CH_2 \quad CH_2}} \xrightarrow{-H_2}$$

$$\left[ \underset{NH}{\bigcirc} \right] - \left| \begin{array}{l} \xrightarrow{+H_2} CH_3CH_2CH_2CH_2NH_2 \\ \\ \xrightarrow{-2H_2} \underset{NH}{\bigcirc} \end{array} \right.$$
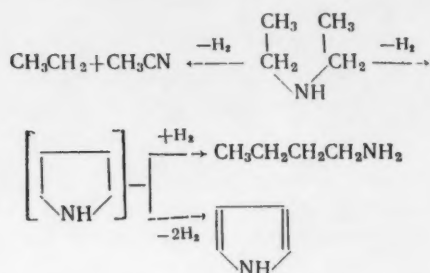
Because it is difficult to visualize another way for the formation of pyrrole and butylamine, one may regard as proven that dehydrocyclization of dialkylamines into pyrolidines takes place.

### EXPERIMENTAL

Platinized carbon (20% of Pt) prepared according to Zelinskii [5] served as the catalyst; diethylamine [b. pt. 55.0-56° (760 mm); $n^{20}D$ 1.3871] was passed over the catalyst at 310° at a velocity of 0.2 $hr^{-1}$ without a carrier gas. The catalyzates had an $n^{20}D$ from 1.3710 to 1.4139. The chromatography of the liquid fraction of catalyzate was conducted in a column 1.5 m. high. As the liquid stationary phase triethanolamine (20%) spread on diato-mite brick was used. The column was equipped with a microflame detector.

### SUMMARY

It was found that when diethylamine is passed over platinized carbon, pyrrole and n-butylamine are formed, i.e., dehydrocyclization takes place which is analogous to the $C_5$-dehydrocyclization of paraffins.

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* The presence of considerable quantities of ethane and hydrogen in the gaseous reaction products was actually established.

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# "RADIOLYTIC OXIDATION OF PROPYLENE WITH OXYGEN"

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We established earlier [1] that under normal conditions the oxidation of ethylene with oxygen under the action of fast electrons passes through the stage of the addition of a molecule of oxygen to the double bond. We report below the results obtained in an investigation of the oxidation of propylene with oxygen in the gas phase.

## EXPERIMENTAL

The experiments were conducted at a potential of an accelerating field amounting to 120 kV, a strength of the discharge current equal to 0.1 mA (total dose 0.55 × 10$^{23}$ eV), an initial pressure corresponding to atmospheric, room temperature, and a ratio of the starting materials equal to 1: 1. The oxidation was carried out in an aluminum chamber with a capacity of 2 l. The liquid products of the reaction which were in the form of a yellow mobile oil, were washed off the walls of the chamber with water. The resulting solution was subjected to analysis.

The carbonyl compounds were precipitated in the form of 2,4-dinitrophenylhydrazones. A mixture was obtained which contained a considerable quantity of osazone. After extraction of the hydrazones from the mixture with hot alcohol, the osazone was purified by passing its solution in pyridine through a column charged with aluminum oxide and subjecting it after this to fractional crystallization. The main fraction had a melting point of 299-300°, which corresponds to the melting point of the dinitrophenylosazone of methyl glyoxal. Found: C 42.12; 42.06; H 2.50; 3.54%. $C_{15}H_{12}N_8O_8$. Calculated: C 41.67; H 2.79%. The other fractions were identical with the principal fraction. However, the solution containing the oxidation product did not give a positive reaction for methyl glyoxal; furthermore, the osazone precipitated very slowly, which is characteristic for an acetol (hydroxyacetone) [2, 3]. One must mention in connection with this that there is information in the literature to the effect that acetol forms as a result of the thermal oxidation of propylene with oxygen [4].

The volatile aldehydes were blown with an air current from the boiling solution into a trap filled with ice water and precipitated with 2,4-dinitrophenylhydrazine. The benzene solutions of the hydrazones was introduced into a column filled with aluminum oxide, whereupon the hydrazones were diluted with a 5% solution of butanol in n-hexane. It was found that the mixture consisted of two hydrazones; however, one of them was contained in the mixture to a very minor extent, so that it was not isolated or identified. The principal hydrazone, after repeated purification on aluminum oxide and recrystallization from methanol, had a melting point of 139-140° which corresponded to that of the dinitrophenylhydrazone of propanal, since this compound occurs in two modifications [5] and on separation from reaction mixtures (but not from the pure aldehyde) may have a lowered melting point [6]. Found: C 44.83; 44.83; H 3.83; 3.93. $C_9H_{10}N_4O_4$. Calculated: C 45.37; H 4.23%. The maximum of absorption of the hydrazone, which was determined in an alcohol solution, coincided with the absorption maximum of the hydrazone of propanal prepared from pure aldehyde; it was located at 359 mµ [7].

Examination by the colorimetric method [8] showed that the oxidation products contained a small quantity of formaldehyde. The acetol was determined quantitatively on the basis of the difference between the total amount of all aldehydes determined by the oxidation of the latter into the corresponding acids [9] and the sum of propioyaldehyde and formaldehyde, under consideration of the error due to the partial oxidation of acetone to $CO_2$ and acetic

acid [10]. The propanal was determined quantitatively on being blown out with a weak air stream from a neutralized solution in a moderate state of boiling. The stream of air was blown through a reflux condensor with a temperature of the cooling water amounting to 30-32°. The blowing was continued for 20 min.; the aldehyde vapor was collected in a bubble trap filled with a 0.5N solution of hydroxylamine hydrochloride. By using this method, a quantity corresponding to 95-96% of the theoretical can be determined.

The total amount of acids was determined by titration with phenolphthaleine. Just as in the case of ethylene, the end point was drawn out because of the presence of peroxides. By employing a method which is specific as far as the analysis of formic acid is concerned [11], we found that the latter comprised the major part of the total acids present and that acids higher than formic were not present in significant quantities. The peroxides were determined iodometrically. Similarly to the ethylene peroxides, the peroxides associated with the oxidation of propylene were formed in considerable quantities and were very unstable to the action of weak alkalis, being converted principally to acids. Propylene oxide was not contained in the oxidation products.

The gaseous products of oxidation were analyzed by chromatography; $CO_2$ and oxygen were determined by the absorption method. The experimental results are listed in the table.

TABLE

| Substance | $G$ | C, % | O, % | Substance | $G$ | C, % | O, % |
|---|---|---|---|---|---|---|---|
| Acetol | 3,5 | 22,6 | 29,5 | $CO_2$ | 0,9 | 2,0 | 7,7 |
| Peroxides | 2,0 | 12,7 | 16,5 | $C_2H_4$ | 0,5 | 2,4 | — |
| Propanal | 1,3 | 8,6 | 5,6 | $C_3H_8$ | 0,9 | 5,9 | — |
| Formaldehyde | 0,2 | 0,4 | 0,8 | $H_2$ | 1,2 | — | — |
| Formic acid | 1,5 | 3,2 | 12,4 | $C_3H_6$ initial | 15,3 | 31,8 | — |
| | | | | $O_2$ initial | 11,7 | — | 22,5 |
| CO | 3,2 | 6,9 | 13,4 | | | | |

Note: G) Yield in molecules/100 eV; C) yield in percent referred to reacted propylene and based on carbon; O) yield in percent based on reacted oxygen.

The data obtained indicated that the principal products of the oxidation of propylene under the action of fast electrons in the gas phase were peroxides, acetol, carbon monoxide, and propionic aldehyde. The absence of acrolein in the oxidation products makes it possible to conclude that allyl hydroperoxide was not formed in noticeable quantities during the oxidation, i.e., there was no oxidation of the methyl group. The high yield of acetol is best explained by the addition of a molecule of oxygen to the double bond of propylene and the isomerization of the cyclic peroxide formed in this manner. This mechanism differs from the generally accepted mechanism of the thermal oxidation of olefins [12], according to which oxidation takes place at the methyl or methylene group located in the $\alpha$-position with reference to the double bond. However, this scheme does not explain satisfactorily the formation of acetol as a primary product. Propionic aldehyde was apparently formed in our experiments as a product of the reaction of propylene peroxide with the initial propylene, while interaction of the primary peroxide with oxygen presumably had to result in complete destruction of the carbon skeleton accompanied by formation of carbon oxides and formic acid. In any event the high yield of carbon monoxide proves that the latter was not a product of the decomposition of formic acid, but was formed parallel to the acid as a primary product. Thus, the scheme of radiolytic oxidation of propylene is essentially analogous to that of the oxidation of ethylene under the effect of fast electrons which has been proposed by us earlier [1].

$$C_3H_6 \rightsquigarrow C_3H_6^* \qquad\qquad C_3H_6^* \xrightarrow{O_2} C_3H_6O_2$$

$$C_3H_6O_2 \rightarrow CH_3COCH_2OH; \qquad C_3H_6O_2 \xrightarrow{C_3H_6} 2C_2H_5CHO.$$
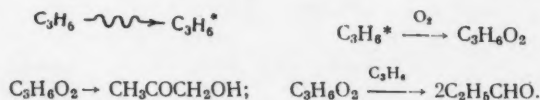
The peroxide indicated in the scheme as $C_3H_6O_2$ apparently has the structure

$$\begin{array}{ccc} CH_3-CH-CH_2 \\ | \quad\quad | \\ O---O \end{array}$$
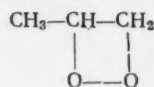
i.e., it is a homolog of the cyclic peroxide of ethylene.

## SUMMARY

1. It was established that radiation-chemical oxidation of propylene with oxygen in the gas phase results mainly in the formation of peroxides, acetol, and carbon monoxide.

2. The mechanism of the principal reaction apparently consists in the addition of an oxygen molecule to the double bond followed by subsequent transformations of the propylene peroxide formed in the manner.

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## "A NEW WAY OF SYNTHESIZING STEROIDS"

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Eschenmoser [1] carried out in 1953 a Michael condensation of 2-methyl-3-vinyl-$\Delta^2$-cyclohexanone (I) with 2-methy-dihydroresorcinol, and as a result of the subsequent cyclization the diketone (II) was formed.
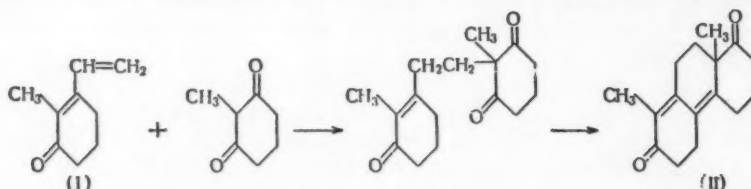


Notwithstanding its simplicity, this procedure for the synthesis of steroids could not be developed further, because no way of building up the A ring was found.

In the work reported at present, a new way of synthesizing steroids is proposed which is based on the application of the reactions mentioned to 2-(γ-ketobutyl)-3-vinyl-Δ²-cyclohexanone (V).

On being boiled with acetic anhydride, 2-(γ-ketobutyl-dihydroresorcinol) (III) was converted into the chromanone (IV), which upon being reacted with vinyl-magnesium bromide and subsequent hydrolysis yielded the dienone (V). After condensation of (V) with 2-methyldihydroresorcinol and cyclization of the intermediate bicyclic compound (VI), which had not been separated in a pure state, the steroid diketone (VII) was obtained, the constitution of which was confirmed by taking ultraviolet spectra of the ketone itself and also of its 2,4-dinitrophenylhydrazone.
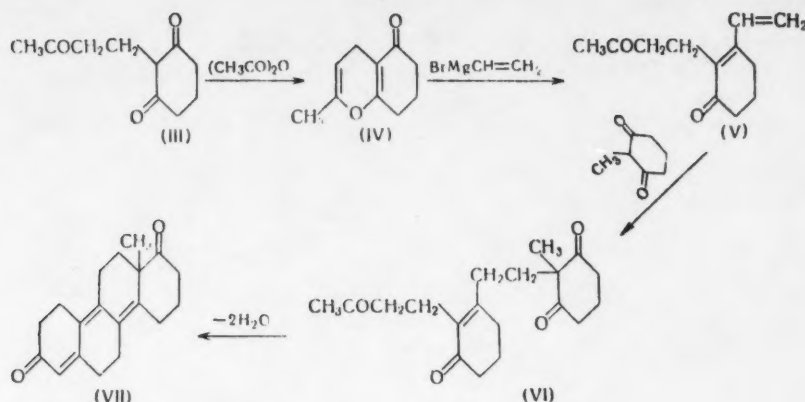


## EXPERIMENTAL

Cyclization of 2-(γ-ketobutyl)-dihydroresorcinol (III). A mixture of 60 gr of unpurified 2-(γ-ketobutyl)-dihydroresorcinol (III) [2] and 150 ml of acetic anhydride was boiled for 3 hours. After the excess of acetic anhydride and acetic acid had been distilled off, the residue was dissolved in 200 ml of ether and then washed with a solution of 15 gr of potassium hydroxide in 200 ml of water in order to remove an admixture of the enol acetate of dihydroresorcinol (II). The ethereal solution was dried with magnesium sulfate. After the solvent had been distilled off, 17.7 gr of chromanone (IV) were obtained; b. pt. 95-96° (2 mm); m. pt. 40-42° (from ether). Found: C 72.81; 72.89; H 7.41; 7.53%. $C_{10}H_{12}O_2$. Calculated: C 73.14; H 7.37%. 2,4-Dinitrophenylhydrazone, m. pt. 197-199°; $\lambda_{max}$ 396 mμ (from alcohol). Found: N 16.54; 16.42%. $C_{16}H_{16}O_5N_4$. Calculated: N 16.27%.

Preparation of 2-(γ-ketobutyl)-3-vinyl-Δ²-cyclohexanone (V). To a Grignard solution prepared from 5.2 gr of magnesium and 20 ml of vinyl bromide in 200 ml of tetrahydrofuran, 17.7 gr of chromanone (IV) in 50 ml of tetrahydrofuran were added under agitation at temperatures from minus 20 to minus 25°. The mixture was kept for one hour at room temperature and then treated successively with 30 gr of ammonium chloride and 100 ml of dilute (2:1) hydrochloric acid under cooling with ice. After the mixture had been let to stand for one hour at room temperature, 15 gr of dienone (V) were extracted with ether; b. pt. 121-124° (2 mm); $n^{19}D$ 1.5410. Found: C 74.74; 74.65; H 8.11; 8.10%. $C_{12}H_{16}O_2$. Calculated: C 75.00; H 8.3%.

Preparation of the steroid diketone (VII). A mixture of 2.5 gr of 2-methyldihydroresorcinol, 0.6 gr of trimethylbenzylammonium chloride, 0.2 gr of potassium hydroxide in 2 ml of methanol and 20 ml of xylene was heated to boiling, whereupon 3.6 gr of dienone (V) in 10 ml of xylene were added. After being boiled for 4 hours, the solution was washed with water and a dilute soda solution was then evaporated to dryness in vacuum (100°, 20 mm). The oil (3.8 gr) which was obtained and which represented the unpurified condensation product (VI), was mixed with 2 ml of pyridine, 2 ml of diethylamine, and 30 ml of xylene. The solution was boiled with the use of a water separator, until the separation of water ceased within 1.5-2 hours. The solution was then cooled, washed with dilute (1:1) hydrochloric acid, and evaporated in vacuum to dryness (100°, 20 mm). The residue was subjected to chromatography on aluminum oxide. From the ether eluate 0.4 gr of the steroid diketone (VII) were separated. This substance crystallized in the form of yellow crystals with a m. pt. of 98-99° from a mixture of heptane and benzene; $\lambda_{max}$ 247.5 mμ (ε 6900); 356 mμ (ε 23800). Found: C 80.89; 80.78; H 7.83; 7.88%. $C_{19}H_{22}O_2$. Calculated: C 80.61; H 7.85%.

2,4-Dinitrophenylhydrazone, m. pt. 135-137°; $\lambda_{max}$ 409 mμ (from alcohol). Found: N 12.51; 12.46%. $C_{25}H_{26}O_5N_4$. Calculated: N 12.12%.

## SUMMARY

A new method for the synthesis of steroids has been found which is based on the Michael condensation of 2-($\gamma$ -ketobutyl)-3-vinyl-$\Delta^2$-cyclohexanone (V) with 2-methyldihydroresorcinol followed by a double cyclization of the tetraketone (VI).

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# "SYNTHESIS OF TAGGED HYDROGEN PEROXIDE FROM HEAVY-WATER VAPOR BY SUBJECTING THE LATTER TO THE ACTION OF A GLOW DISCHARGE"

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We carried out a synthesis of $H_2O_2^*$ in a glow discharge from $H_2O^*$ vapor which contained $1.75 \pm 0.01$ atomic percent of $O^{18}$. The vapor was withdrawn from the discharge zone and frozen out in a trap cooled with liquid nitrogen. The equipment used by us was described in the article [1]. The vitreous substance that had been frozen out in the trap contained on melting 28.4% by weight of $H_2O_2$. The content of $O^{18}$ in this peroxide was found to be equal to $1.82 \pm 0.01$ atomic percent (mean value obtained by 35 mass-spectrometric determinations on 5 samples.) enrichment coefficient was 1.04.

This method for the synthesis of $H_2O_2^*$ is more convenient than that which has been described in the literature earlier, because it makes it possible to prepare directly $H_2O_2^*$ which has a sufficiently high degree of concentration and sufficient purity.

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# "NEW METHODS FOR THE SYNTHESIS OF ESTERS OF ALKYLBORIC ACIDS"

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In the course of investigating the properties of the tetraalkyldiboranes prepared by us earlier [1], we found a new method for the preparation of esters of alkyl boric acid. It was found that tetraalkyldiboranes react with orthoborates with the formation of esters of alkylboric acid (with a yield of 80-90%), this reaction taking place slowly at room temperature and rapidly on heating to 80-100°.

$$R_4B_2H_2 + 2(R'O)_3B \rightarrow 3RB\,(OR')_2 + \tfrac{1}{2}R_2B_2H_4$$
$$R = n\text{-}C_3H_7,\ n\text{-}C_4H_9;\ R' = CH_3,\ n\text{-}C_3H_7,\ n\text{-}C_7H_{15} \tag{1}$$
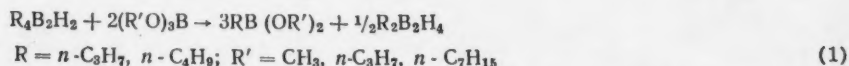
Reaction (I) proceeds over a number of intermediate stages of the replacement of hydrogen with alkyl and alkoxy groups in the tetraalkyldiboranes and their primary conversion products. We established further that the dialkyldiboranes reacted with trialkyl boron (with particular facility on heating) under the formation of tetraalkyldiboranes

$$R_2B_2H_4 + 2R_3B \rightarrow 2R_4B_2H_2$$
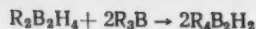
The fact that the dialkyldiboranes which are found by reaction (I) are converted into tetraalkyldiboranes in the presence of trialkylboron, enables us to synthesize esters of alkyl boric acids from alkyl boranes and ortho-borates in the presence of small quantities of tetraalkyldiboranes which exerted a catalytic effect. By heating a mixture of the substances mentioned at 80-100°

$$R_3B + 2(R'O)_3B \xrightarrow{R_4B_2H_2} 3RB(OR')_2$$
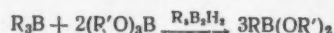
we prepared different esters of alkylboric acids with yields of 80-90%.

## LITERATURE CITED

1. B. M. Mikhailov, A. A. Akhnazaryan, and L. S. Vasil'ev, Dokl. AN SSSR 136, 828 (1961).

# "ORGANOLITHIUM VINYLBENZENES HALOGENATED IN THE SIDE CHAIN AND SOME OF THEIR REACTIONS"

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L. Ya. Karpov Phys. Chem. Inst.

By means of the double exchange reaction

$$CX_2{=}CXC_6H_4Br + C_4H_9Li \rightarrow CX_2{=}CXC_6H_2Li + C_4H_9Br$$

(where X is F or Cl) carried out in ether at a low temperature, we were able to synthesize organolithium vinylbenzenes halogenated in the side chain. We investigated some of the reactions of compounds of this type. As examples we may cite the following transformation of the novel ArLi compounds:

1. Treatment with carbon monoxide resulted in the formation of ArCOOH (where Ar is $CClF = CFC_6H_4-$), m.pt. 165-166°. Found: C 49.49; 49.59; H 2.26; 2.32; Cl 16.16; 16.39%. Calculated: C 49.43; H 2.29; Cl 16.25%.

2. Interaction of ArLi with $HgBr_2$ resulted in the formation of ArHgBr, m. pt. 221-223°. Found: Hg 44.80%; sum of Cl and Br 24.96; 25.18. Calculated: Hg 44.18%; sum of Cl and Br 25.40.

3. Interaction of ArLi with $(C_2H_5)SnCl$ resulted in the formation of $ArSn(C_2H_5)_3$, b. pt. 170° (4 mm). Found: Sn 31.16; 31.15; Cl 9.76; 9.90%. Calculated: Sn 31.28; Cl 9.36%.

4. Upon reaction with acetaldehyde, divinylbenzene was obtained which was halogenated at one of the vinyl groups.

Low temperatures (about minus 70°) were found necessary for carrying out the reactions mentioned above and also for reactions with halides of other elements or other organoelemental compounds. The novel aryl lithium compounds synthesized by us were found to be capable of undergoing the total diverse range of reactions typical for organolithium compounds. The monomers prepared by us were capable of polymerization. It is of interest to note that when the temperature was allowed to rise during the preparation of the new aryl lithium compounds or the reaction was prolonged, one arrived at polycondensation products of the $(-CX = CXC_6H_4-)$ type, which are of interest to us from another standpoint.

# Soviet Journals Available in Cover-to-Cover Translation

| ABBREVIATION | RUSSIAN TITLE | TITLE OF TRANSLATION | PUBLISHER | Vol. | Issue | Year |
|---|---|---|---|---|---|---|
| AÉ | Atomnaya énergiya | Soviet Journal of Atomic Energy | Consultants Bureau | 1 | 1 | 1956 |
| Akust. zh. | Akusticheskii zhurnal | Soviet Physics – Acoustics | American Institute of Physics | 1 | 1 | 1955 |
| | Antibiotiki | Antibiotics | Consultants Bureau | 4 | 1 | 1959 |
| Astr(on). zh(urn). | Astronomicheskii zhurnal | Soviet Astronomy—AJ | American Institute of Physics | 34 | 1 | 1957 |
| Avto(mat). svarka | Avtomaticheskaya svarka | Automatic Welding | British Welding Research Association (London) | | | |
| | Avtomatika i Telemekhanika | Automation and Remote Control | Instrument Society of America | 27 | 1 | 1959 |
| | Biofizika | Biophysics | National Institutes of Health* | | 1 | 1956 |
| | Biokhimiya | Biochemistry | Consultants Bureau | 21 | 1 | 1957 |
| Byull. éksp(erim). biol. i med. | Byulleten' éksperimental'noi biologii i meditsiny | Bulletin of Experimental Biology and Medicine | Consultants Bureau | 41 | 1 | 1959 |
| DAN (SSSR) / Dok(lady) AN SSSR | Doklady Akademii Nauk SSSR | The translation of this journal is published in sections, as follows: | | | | |
| | | **Life Sciences** — Doklady Biochemistry Section | American Institute of Biological Sciences | 106 | 1 | 1956 |
| | | Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections) | American Institute of Biological Sciences | 112 | 1 | 1957 |
| | | Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections) | American Institute of Biological Sciences | 112 | 1 | 1957 |
| | | **Chemical Sciences** — Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology | Consultants Bureau | 106 | 1 | 1956 |
| | | Proceedings of the Academy of Sciences of the USSR, Section: Chemistry | Consultants Bureau | 106 | 1 | 1956 |
| | | Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry | Consultants Bureau | 112 | 1 | 1957 |
| | | **Earth Sciences** — Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections) | American Geological Institute | 124 | 1 | 1959 |
| | | Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry | Consultants Bureau | 106-123 | 6 | 1957-1958 |
| | | Proceedings of the Academy of Sciences of the USSR, Sections: Geology | Consultants Bureau | 106-123 | 1 | 1957-1958 |
| | | **Mathematics** — Doklady Soviet Mathematics | The American Mathematics Society | 131 | 6 | 1961 |
| | | **Physics** — Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections) | American Institute of Physics | 106 | 1 | 1956 |
| | | Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections) | Consultants Bureau | 106-117 | 1 | 1956-1957 |
| Derevoobrabat. prom-st'. | Derevoobrabatyvayushchaya promyshlennost' | Wood Processing Industry | Timber Development Association (London) | | | |
| Élecktrosvyaz | Élecktrosvyaz | Telecommunications | Massachusetts Institute of Technology* | | 9 | 1959 |
| Éntom(ol). oboz(renie) | Éntomologicheskoe obozrenie | Entomological Review | American Institute of Biological Sciences | 38 | 1 | 1959 |
| Farmakol. (i) toksikol(ogiya) | Farmakologiya i toksikologiya | Pharmacology and Toxicology | Consultants Bureau | 20 | 1 | 1957 |
| FMM | Fizika metallov i metallovedenie | Physics of Metals and Metallography | Acta Metallurgica* | 5 | 1 | 1957 |
| Fiziol. zhurn. SSSR (im. Sechenova) | Fiziologicheskii zhurnal im. I. M. Sechenova | Sechenov Physiological Journal USSR | National Institutes of Health* | | 1 | 1957 |
| Fiziol(ogiya) rast. | Fiziologiya rastenii | Plant Physiology | American Institute of Biological Sciences | 4 | 1 | 1957 |
| | Geokhimiya | Geochemistry | The Geochemical Society | | 1 | 1958 |
| FTT | Fizika tverdogo tela | Soviet Physics—Solid State | American Institute of Physics | 1 | 1 | 1959 |
| Izmerit. tekh(nika) | Izmeritel'naya tekhnika | Measurement Techniques | Instrument Society of America | | 1 | 1959 |
| Izv. AN SSSR, O(td). Kh(im). N(auk) | Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk | Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences | Consultants Bureau | | 1 | 1952 |

*continued*

| Abbreviation | Title (transliterated Russian) | Title (English) | Sponsoring organization | | | Year |
|---|---|---|---|---|---|---|
| Izv. AN SSSR, O(td). T(ekhn). N(auk); Met(all). i top. | (see Met. i top.) | | | | | |
| Izv. AN SSSR Ser. fiz(ich). | Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya | Bulletin of the Academy of Sciences of the USSR: Physical Series | Columbia Technical Translations | | 1 | 1954 |
| Izv. AN SSSR Ser. geofiz. | Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya | Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series | American Geophysical Union | | 1 | 1954 |
| Izv. AN SSSR Ser. geol. | Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya | Izvestiya of the Academy of Sciences of the USSR: Geologic Series | American Geological Institute | | 1 | 1958 |
| Kauch. i rez. | Kauchuk i rezina | Soviet Rubber Technology | Research Association of British Rubber Manufacturers | | | |
| | Kinetika i kataliz | Kinetics and Catalysis | Consultants Bureau | 18 | 1 | 1959 |
| | Koks i khimiya | Coke and Chemistry USSR | Coal Tar Research Association (Leeds, England) | 1 | 3 | 1960 |
| Kolloidn. zh(urn). | Kolloidnyi zhurnal | Colloid Journal | Consultants Bureau | 14 | 1 | 1958 |
| | Kristallografiya | Soviet Physics – Crystallography | American Institute of Physics | 2 | 1 | 1952 |
| Metalov. i term. obrabot. metal. | Metallovedenie i termicheskaya obrabotka metallov | Metal Science and Heat Treatment of Metals | Acta Metallurgica | 6 | 1 | 1957 |
| | Metallurg | Metallurgist | Acta Metallurgica | | 1 | 1958 |
| Met. i top. | Metallurgiya i topliva | Russian Metallurgy and Fuels | Eagle Technical Publications | 26 | 1 | 1957 |
| Mikrobiol. | Mikrobiologiya | Microbiology | American Institute of Biological Sciences | | 1 | 1960 |
| OS | Optika i spektroskopiya | Optics and Spectroscopy | American Institute of Physics | | 6 | 1957 |
| | Pochvovedenie | Soviet Soil Science | American Institute of Biological Sciences | | 1 | 1959 |
| | Priborostroenie | Instrument Construction | British Scientific Instrument Research Association | | 1 | 1958 |
| Pribory i tekhn. éks(perimenta) | Pribory i tekhnika éksperimenta | Instruments and Experimental Techniques | Instrument Society of America | | 1 | 1959 |
| Prikl. matem. i mekh. | Prikladnaya matematika i mekhanika | Applied Mathematics and Mechanics | American Society of Mechanical Engineers | | 1 | 1957 |
| PTÉ | (see Pribory i tekhn. éks.) | | | | | |
| | Problemy Severa | Problems of the North | National Research Council of Canada | | 1 | 1958 |
| Radiotekh. | Radiotekhnika | Radio Engineering | Massachusetts Institute of Technology* | 12 | 1 | 1957 |
| Radiotekh. i élektronika | Radiotekhnika i élektronika | Radio Engineering and Electronics | Massachusetts Institute of Technology* | 2 | 1 | 1957 |
| | Stanki i instrument | Machines and Tooling | Production Engineering Research Assoc. | | 1 | 1959 |
| Stek. i keram. | Stal' | Stal' (in English) | Iron and Steel Institute | | 1 | 1959 |
| | Steklo i keramika | Glass and Ceramics | Consultants Bureau | | 1 | 1958 |
| Svaroch. proiz-vo | Svarochnoe proizvodstvo | Welding Production | British Welding Research Association | | 1 | 1959 |
| Teor. veroyat. i prim. | Teoriya veroyatnostei i ee primenenie | Theory of Probability and Its Applications | Society for Industrial and Applied Mathematics | 13 | 4 | 1959 |
| Tsvet. Metally | Tsvetnye metally | Nonferrous Metals | Primary Sources | | 1 | 1956 |
| UFN | Uspekhi fizicheskikh Nauk | Soviet Physics – Uspekhi (partial translation) | American Institute of Physics | 66 | 1 | 1960 |
| UKh | Uspekhi khimii | Russian Chemical Reviews | The Chemical Society (London) | | 1 | 1958 |
| UMN | Uspekhi matematicheskikh nauk | Russian Mathematical Surveys | London Mathematical Society | 15 | 1 | 1960 |
| Usp. fiz. nauk | (see UFN) | | | | | |
| Usp. khim(ii) | (see UKh) | | | | | |
| Usp. matem. nauk | (see UMN) | | | | | |
| Usp. sovr. biol. | Uspekhi sovremennoi biologii | Russian Review of Biology | Oliver and Boyd | 48 | | 1959 |
| Vest. mashinostroeniya | Vestnik mashinostroeniya | Russian Engineering Journal | Production Engineering Research Assoc. | 4 | | 1959 |
| Vop. gem. i per. krovi | Voprosy gematologii i perelivaniya krovi | Problems of Hematology and Blood Transfusion | National Institutes of Health* | | 1 | 1957 |
| Vop. onk. | Voprosy onkologii | Problems of Oncology | National Institutes of Health* | | 1 | 1957 |
| Vop. virusol. | Voprosy virusologii | Problems of Virology | National Institutes of Health* | | 1 | 1957 |
| Zavodsk). lab(oratoriya) | Zavodskaya laboratoriya | Industrial Laboratory | Instrument Society of America | 25 | 1 | 1959 |
| ZhAKh Zh. anal(it). khimii | Zhurnal analiticheskoi khimii | Journal of Analytical Chemistry USSR | Consultants Bureau | 7 | 1 | 1952 |
| ZhETF Zh. éksperim. i teor. fiz. | Zhurnal éksperimental'noi i teoreticheskoi fiziki | Soviet Physics–JETP | American Institute of Physics | 28 | 1 | 1955 |
| ZhFKh Zh. fiz. khimii | Zhurnal fiz. khimii | Russian Journal of Physical Chemistry | The Chemical Society (London) | 7 | 7 | 1959 |
| ZhMEi Zh(urn). mikrobiol. épidemiol. i immunobiol. | Zhurnal mikrobiologii, épidemiologii i immunobiologii | Journal of Microbiology, Epidemiology and Immunobiology | National Institutes of Health* | | 1 | 1957 |
| ZhNKh Zh(urn). neorgan(ich). khimii | Zhurnal neorganicheskoi khimii | The Russian Journal of Inorganic Chemistry | The Chemical Society (London) | | 1 | 1959 |
| ZhOKh Zh(urn). obshch(ei) khimii | Zhurnal obshchei khimii | Journal of General Chemistry USSR | Consultants Bureau | 19 | 1 | 1949 |
| ZhPKh Zh(urn). prikl. khimii | Zhurnal prikladnoi khimii | Journal of Applied Chemistry USSR | Consultants Bureau | 23 | 1 | 1950 |
| ZhSKh Zh(urn). strukt. khimii | Zhurnal strukturnoi khimii | Journal of Structural Chemistry | Consultants Bureau | 1 | 1 | 1960 |
| ZhTF Zh(urn). tekhn. fiz. | Zhurnal teknicheskoi fiziki | Soviet Physics–Technical Physics | American Institute of Physics | 26 | 1 | 1956 |
| Zh(urn). vyssh. nervn. deyat. (im. Pavlova) | Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova) | Pavlov Journal of Higher Nervous Activity | National Institutes of Health* | | 1 | 1958 |

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.

BORIS ALEKSANDROVICH KAZANSKII

Dear Boris Aleksandrovich!

The Presidium of the Academy of Sciences of the USSR, the Department of Chemical Sciences, and the Editor of the journal "Izvestiya AN SSSR, Otdelenie Khimicheskikh Nauk" heartily congratulate you on your seventieth birthday and forty years of scientific, pedagogical, and public activities.

You have contributed greatly to chemical science with your profound studies. The distinguishing feature of your studies is their inseparable link with the practice and solution of national-economic problems. You inseparably link your scientific activities with teaching, devoting much energy to the training of highly skilled specialist-chemists.

For many years you have been in charge of a vast and responsible scientific organization, directing the N. D. Zelinskii Institute of Organic Chemistry. You befittingly represent Soviet Science in the International Union for Pure and Practical Chemistry.

The Soviet Government, highly appreciative of your services, have rewarded you with the Order of Lenin, the Order of Illustrious Red Workers, and the conferment of the Stalin Prize.

We wish you, dear Boris Aleksandrovich, good health and further fruitful activity.

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THE PRESIDIUM OF THE ACADEMY OF
SCIENCES USSR,
THE DEPARTMENT OF CHEMICAL SCIENCES
OF THE ACADEMY OF SCIENCES USSR,
THE EDITOR OF THE JOURNAL
"IZVESTIYA AN SSSR, OTDELENIE KHIMICHESKIKH NAUK"

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